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# HIGH POLYMERIC CHEMISTRY



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*by*

W. S. PENN

B.Sc.



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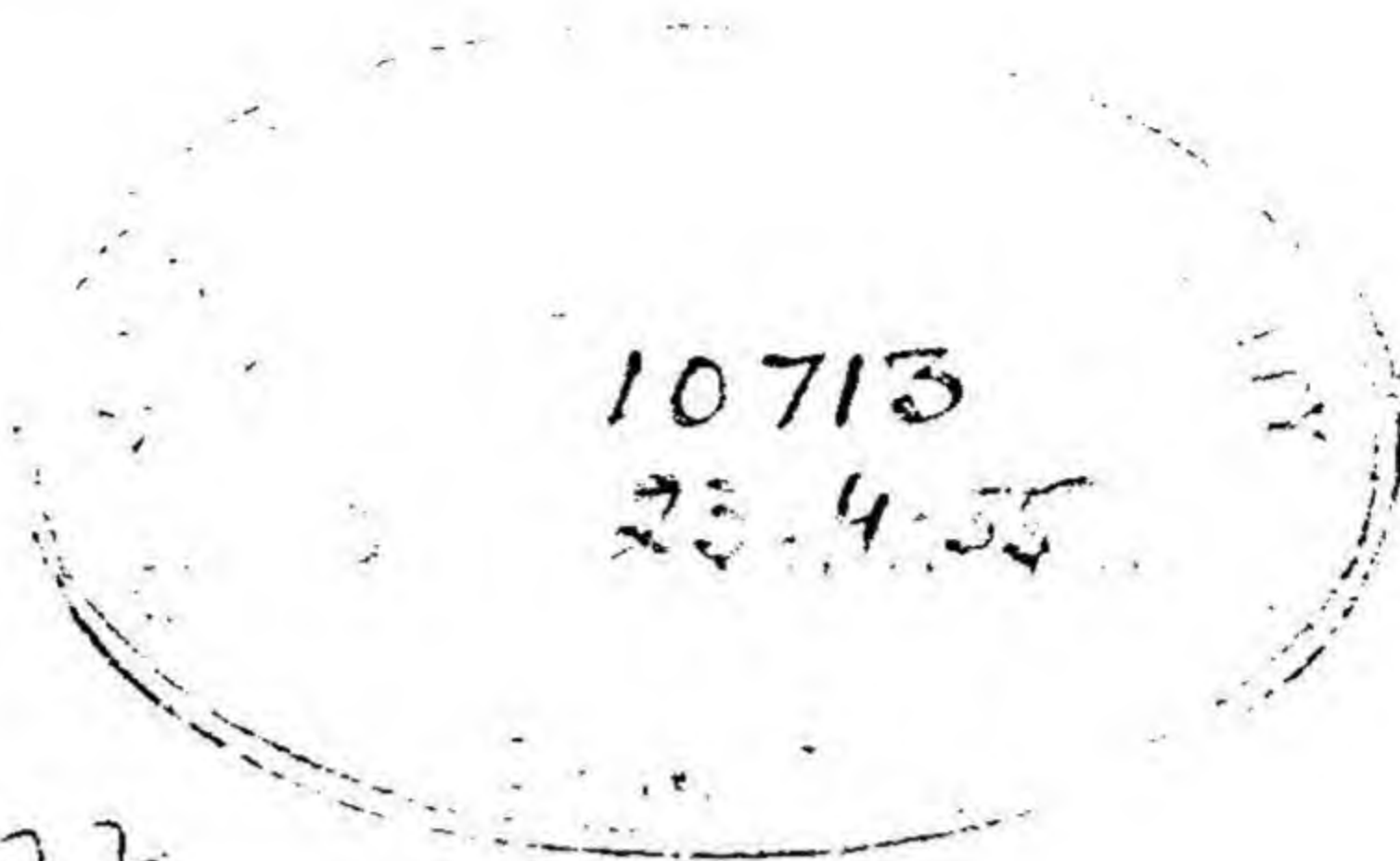
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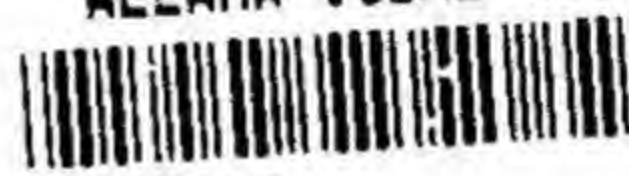
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## PREFACE TO SECOND EDITION

Our "Laboratory Manual of Elementary Physical Chemistry" was written primarily for the use of our own students in the laboratories of The Ohio State University. If teachers in other institutions find any appealing pedagogic values in our manual, we are very happy to have them and their students use it. We have seized the occasion for a second edition as an opportunity to adopt many of the suggestions made to us by friends to improve and enlarge the manual.

A course in physical chemistry laboratory work may, in general, shape itself along either one of two different lines. The student may be required to build his own apparatus, blow the glass, calibrate the flasks and weights, purify the working substances, prepare the standard solutions, etc. Manipulative skill acquired in this way is indeed invaluable, not only for its own sake, but also because it leads the student to an increasing confidence in his own abilities. Every opportunity should be given for the development of such skill. But with a limited amount of time available, the student could not hope to complete any great number or variety of experiments. In this manual the plan has been adopted of having much of the equipment made ready for immediate assembly and most of the working substances already prepared for use, so that the student may cover as much ground as possible. The acquirement of some manipulative skill is thus sacrificed in the attempt to introduce a larger number of laboratory illustrations of the underlying principles of physical chemistry. However, a number of experiments particularly adapted to giving the student some considerable practice in the laboratory arts is included. For such matters as the calibration of weights, of flasks, of pipettes, of burettes, the construction of thermostats, etc., the student is referred to other manuals in which details of the proper procedure have been adequately given.

Among the most important objectives in a laboratory course in physical chemistry must be counted the acquirement of some



ability and if possible some skill, on the part of the student, in the interpretation and mathematical treatment and reduction of the results of an experiment. The importance of this matter can hardly be over-emphasized. While it is sometimes true that scientific investigators seem able to draw conclusions from data which do not inherently and justifiably lead to such conclusions at all, it is perhaps more generally true that many interesting and important deductions which might have been and should have been crystallized out, are missed altogether.

Therefore, in our manual, while we give plenty of opportunity for the student to acquire useful experimental techniques, we have put particular emphasis on the underlying principles, and have illustrated repeatedly some of the more common and powerful mathematical approaches to a discussion of results, such as the Boltzmann factor treatment. Nor have we hesitated to supply a good deal of theoretical background at some of the more troublesome points in the interpretation and argument; although we must naturally depend on references to some of the widely used text-books in physical chemistry and on other references for the development of any complete or extensive theoretical treatment.

We cannot make a claim that any research spirit, even of the most primitive sort, has been infused into our descriptions and directions for procedure; but as far as the subject matter would permit, we have at least attempted to make the experiments into *projects*, rather than routine tasks. We hope that the student will approach his work in this spirit.

E. M. Jr.  
W. G. F.

*January 18, 1934.*



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## EXERCISE I

### UNITS AND DIMENSIONS

(A) **Units.** Van't Hoff defined physical chemistry as the attempt to employ the methods of physics in the study of chemistry, with the hope of benefiting the latter. Physics was at one time, and is today, in many respects, a more exact science than chemistry, and this is to be expected, since the problems in whose solution the physicist is interested generally involve a smaller number of variable factors than the problems of chemistry. For the same reason chemistry is a more exact science than physiology, or psychology, or sociology. However, many of the problems of physics and chemistry are mutual ones, and in the strenuous modern endeavor to solve them, physics and chemistry are being drawn so closely together that it is impossible to say where one stops and the other begins.

The things which are measured, both in physics and in chemistry, are *measurable properties or quantities*, such as, length, viscosity, quantity of electric charge, mass, velocity, temperature, etc. There are, at the present time, several score of such quantities known, and from time to time new ones are added to the list. For instance, the physical quantities met with in a study of heat, namely, temperature, quantity of heat, specific heat, entropy, heat conductivity, heat emissivity, etc., have all been added to the list during the past few hundred years as a result of the gradual refinement of a rather vague notion that people used to entertain about degrees of hotness and coldness (mere physiological sensations).

Every experiment in measurement involves a method of sifting out or identifying the particular quantity studied, and a scheme of scaling it with reference to a standard. The counterparts in the record or expression of the measurement are then (1) the name of the quantity measured, (2) the indication of the unit or standard specimen, and (3) the number value which gives the number of times the unit is contained in the quantity measured. The num-



ber is given to the proper significant figure, so that the accuracy of the measurement is neither over-stated nor under-stated; the selection of the unit is generally controlled by convenience or custom, and the particular choice is less important than the absence of ambiguity in its description.

A perfectly feasible system of units could be established by defining arbitrarily and placing in a bureau of standards a separate unit for each one of the measurable quantities. Thus, the arbitrarily chosen length of a certain line might be defined as the unit of length, and the area of a certain square, not necessarily bearing any simple relationship to the unit of length, might be taken as the unit of area. (Of course, the choice of figure is not necessarily limited to a *square*.) Similarly the volume of a certain vessel might be the unit of volume, a certain dry cell might furnish the unit of electromotive force, the viscosity of a certain oil or syrup the unit of viscosity, etc. There would then be as many arbitrarily defined units as there are measurable quantities.

As a matter of fact, however, we set up only three or four or five arbitrarily defined units in our bureau of standards and *derive* all the others. The very possibility of doing this depends upon the existence of a *sufficient number of experimentally established* relationships among the measurable quantities, relationships which are our natural physical laws. For example, one of these relationships is the well-known law that velocity is directly proportional to length and inversely proportional to time, or using symbols to represent the physical quantities,  $v = k \times \frac{l}{t}$ , where  $k$  is a proportionality constant. This equation relates velocity to length and time. Another such relationship is Ohm's law,  $i = k \times \frac{e}{r}$ , where  $i$  represents the physical quantity strength of current,  $e$  the electromotive force, and  $r$  the resistance.

For the sake of making clear some of the points involved in the theory of units and dimensions, let us assume, to begin with, that there are only three physical quantities known, length, area and volume. There are only two independent relationships among these three quantities, namely,  $A = k \times l^2$ , and  $V = k \times l^3$ . (Of course,  $k$  is a universal constant only for some particular shape.) It is true that there is another relationship,  $V = k \times A^{\frac{3}{2}}$ , but it



is not an independent one, as it follows directly from the other two. If, now, we arbitrarily define the unit of any one of these three quantities, length, area and volume, the units of the others may be derived by virtue of the existence of the two relationships. Let us select length and arbitrarily define the unit of length as  $1/100$  of the distance between two marks on a certain bar of platinum kept at the standard temperature in a museum in Paris. We thus arbitrarily set up the centimeter, unit of length in the c.g.s. system. Taking now the equation  $A = k \times l^2$ , we may define the unit of area so that the proportionality constant becomes equal to 1 (one) for some particular chosen and specified shape of figure, and we may choose for the unit of area a square with edge one centimeter long. Then  $A = l^2$ , and it follows that the measure in units of area of any square surface of whatever size is not only proportional to, but is *numerically equal* to the square of its edge, measured in centimeters. Similarly, taking the equation  $V = k \times l^3$ , we may define the unit of volume in such a way that  $k$  becomes equal to 1. This gives us the cubic centimeter as the derived unit of volume.

If, then, we have three physical quantities, with two relationships existing among them, we need define arbitrarily the unit of only one. Except for convenience, it makes no difference which one of the three we select; the unit of area or the unit of volume may just as well be selected for arbitrary definition as the unit of length.

Let us suppose that a fourth physical quantity, linear curvature, is introduced and is added to the list of three already known. Since the curvature is inversely proportional to length (of radius),  $\rho = k \times \frac{1}{l}$ , the *existence of this relationship* makes it possible to define the unit of curvature (making  $k = 1$ ), without adding an arbitrary unit to the museum. But if now a fifth quantity, time, be added, an arbitrary definition of the unit of time must be given since there is no known relationship\* involving merely time and

\* This statement is not strictly true. The present system of fundamental units was established before relativity, and there was then no known relationship of the required type between space and time measurements. Similarly, the first sentence of the next paragraph should be qualified. In curved-space relativity, mass is related to curvature and hence to length.

In this general connection, however, it is well to bear in mind that certain relationships may be primarily accepted but not utilized for the reduction of units on account of the too meager accuracy of the measurements involved.



any one or more of the quantities length, area, volume and curvature. The unit of time, the second, is taken as  $1/86,400$  of a mean solar day. When the physical quantities velocity and acceleration appear, their units, cm. per sec. and cm. per sec. per sec., may be derived since laws are known relating them to length and time, namely  $v = k \times \frac{l}{t}$ , and  $a = k \times \frac{l}{t^2}$ .

The unit of mass, when this quantity is added to the list, must be defined arbitrarily, since we find that there is no relationship connecting mass with any of the foregoing quantities. The unit of mass, in the c.g.s. system, is set up as  $1/1000$  part of a certain mass of platinum kept in Paris. When the quantity force and the relationship  $f = k \times m \times a$ , or its equivalent  $f = k \times m \frac{l}{t^2}$ , are added to the list, the unit of force (to which is assigned the name dyne) may be derived by defining it as that force which when acting on a mass of one gram for one second will increase its velocity one centimeter per second. This unit of force when substituted in the equation just given would of course make the proportionality constant equal to 1, so that the equation would become  $f = \frac{m \times l}{t^2}$ . In the same way, the erg, the unit of energy, may be derived from the relationship  $E = k \times \frac{m \times l^2}{t^2}$ .

We now have a list of ten quantities, length, area, volume, curvature, time, velocity, acceleration, mass, force and energy; and seven independent relationships. Three units have been defined arbitrarily and seven have been derived. Whenever a new quantity is added without a corresponding relationship, another arbitrary unit must be defined, but when the new quantity is related to the other quantities by a physical law, its unit may be derived. Reasoning inductively from these few illustrations we may conclude that if  $n$  equals the number of known measurable quantities and  $n'$  equals the number of relationships existing among them then  $n - n'$  gives the number of units to be defined arbitrarily. In the three domains of (1) *geometry*, which deals with space, and (2) *kinematics*, which deals with space and time, and (3) *mechanics*, which deals with space, time and mass, there are, we may say for the sake of specific illustration, 51 quan-



tities known and 48 relationships existing among them. (Here again we are taking the pre-relativity point of view.) Hence the units of 3 physical quantities must be arbitrarily defined, the so-called "three fundamental units." As already intimated, however, it is not at all essential to this scheme that the units of length, time and mass be selected for arbitrary definition. We may just as well select length, time and force, or length, time and energy, or other combinations of three.

When, however, we enter the domain of thermal quantities it seems best to define the unit of temperature arbitrarily, because of the absence of a sufficiently well established experimental relationship between temperature and other measurable quantities, and also because, as previously indicated, it may be wise, on the score of accuracy, to have a larger number of fundamental units than is theoretically sufficient. Likewise, in the domains of electricity and magnetism, a more satisfactory and consistent scheme of units is obtained by arbitrary choice of a single fundamental electro-magnetic unit, for example, electric charge, although the common systems choose either dielectric constant or magnetic permeability.

**(B) Dimensions.** In deriving the unit of area in the previous section, it is defined as the area of a square of one centimeter edge, or the unit of area is equal to the unit of length squared. The unit of area may then be said to have the dimensions of length squared  $[L^2]$ . Similarly, since the unit of volume is equal to the unit of length cubed, the unit of volume is said to have the dimensions of length cubed  $[L^3]$ . Since the unit of velocity is made up of a unit of length divided by a unit of time the dimensions of a unit of velocity are  $[L \div T]$ , or  $[LT^{-1}]$ . For a unit of acceleration we have the dimensions  $[LT^{-2}]$ , for a unit of force  $[LT^{-2}M]$ , etc. Dimensional formulas of this sort indicate the exponents of the primary units which enter into the derived units. Not only the units but the physical quantities themselves may be said to have the dimensions indicated. Thus, any force, of whatever size, has the dimensions, in terms of length, mass and time, of  $[LT^{-2}M]$ .

The dimensions of a number of physical quantities are given in the following table.



TABLE I

Quantity	Dimensions	Quantity	Dimensions
Length.....	[L]	Force, weight.....	[LT <sup>-2</sup> M]
Area.....	[L <sup>2</sup> ]	Energy.....	[L <sup>2</sup> T <sup>-2</sup> M]
Volume.....	[L <sup>3</sup> ]	Power.....	[L <sup>2</sup> T <sup>-3</sup> M]
Curvature.....	[L <sup>-1</sup> ]	Momentum.....	[LT <sup>-1</sup> M]
Time.....	[T]	Pressure.....	[L <sup>-1</sup> T <sup>-2</sup> M]
Velocity.....	[LT <sup>-1</sup> ]	Density.....	[L <sup>-3</sup> M]
Acceleration.....	[LT <sup>-2</sup> ]	Specific volume.....	[L <sup>3</sup> M <sup>-1</sup> ]
Mass.....	[M]	Surface tension.....	[T <sup>-2</sup> M]
		Viscosity.....	[L <sup>-1</sup> T <sup>-1</sup> M]

If the unit of temperature be defined arbitrarily, then the dimensions of temperature are  $[\theta]$ . Quantity of heat has the dimensions of energy  $[L^2T^{-2}M]$ , and hence entropy has the dimensions  $[L^2T^{-2}M\theta^{-1}]$ . The dimensions of some of the thermal quantities are listed in the following table.

TABLE II

Quantity	Dimensions	Quantity	Dimensions
Temperature.....	$[\theta]$	Specific heat.....	$[L^2T^{-2}\theta^{-1}]$
Quantity of heat....	$[L^2T^{-2}M]$	Thermal conductiv-	
Entropy.....	$[L^2T^{-2}M\theta^{-1}]$	ity.....	$[LT^{-3}M\theta^{-1}]$
Thermal capacity... $[L^2T^{-2}M\theta^{-1}]$		Gas constant.....	$[L^2T^{-2}M\theta^{-1}]$

Finally when we attempt to set up a consistent scheme of dimensions for electrical and magnetic quantities, several different procedures are possible. For example, Coulomb's law

$$f = k \times \frac{q_1 \times q_2}{D \times l^2}$$

relates the two electrical charges  $q_1$  and  $q_2$  to the square of the distance  $l$  separating them and the force  $f$  exerted between them.  $k$  is a proportionality constant and  $D$  is the dielectric constant.  $q_1$  and  $q_2$  may be made equal, and of such a size that  $k$  becomes equal to 1 for unit force, unit length and unit dielectric constant. This defines the derived unit of charge. Its dimensions, then, are  $[\sqrt{LT^{-2}M \times L^2 \times D}]$ , which reduces to  $[L^{\frac{1}{2}}T^{-1}M^{\frac{1}{2}}D^{\frac{1}{2}}]$ , and the unit of  $D$ , the dielectric constant, must then be defined arbitrarily. Since current is proportional to charge and inversely proportional to time, the dimensions of current are  $[L^{\frac{1}{2}}T^{-2}M^{\frac{1}{2}}D^{\frac{1}{2}}]$ . Since electrical energy is proportional to the product of charge and



potential, the dimensions of electrical potential are

$$[L^2T^{-2}M \text{ (energy)} \div L^{\frac{1}{2}}T^{-1}M^{\frac{1}{2}}D^{\frac{1}{2}}],$$

which is equivalent to  $[L^{\frac{1}{2}}T^{-1}M^{\frac{1}{2}}D^{-1}]$ . From the relationship between resistance and potential and current (Ohm's law) it can be shown that the dimensions of resistance are  $[L^{-1}TD^{-1}]$ , and of conductance  $[LT^{-1}D]$ . In some text-books of physics, it is assumed that the dielectric constant is dimensionless, and the above dimensions are given without the D. Such an assumption is, however, certainly unjustifiable.

It is to be noted that the dimensions just given are for electrostatic units. If, as in the electro-magnetic system, the unit of magnetic permeability is chosen for arbitrary definition, then the dimensions of the electromagnetic unit of charge are  $[L^{\frac{1}{2}}M^{\frac{1}{2}}\mu^{-1}]$ , where  $\mu$  is permeability. The dimensions of the other quantities may then be expressed in terms of  $LTM\mu$ , by a procedure similar to that employed for the derivation of the dimensions of electrostatic units.

It is also possible to follow the suggestion of certain physicists, and adopt the unit of *electric charge* for arbitrary definition. If this is done, the fractional exponents of the dimensions, as given above, disappear. The following table lists the dimensions of a number of electrical and magnetic quantities, worked out on this basis. The student should check carefully the dimensions of each quantity, and if necessary he should refresh his memory of the equational relationships involved by consultation of a good text-book of physics.

TABLE III

Quantity	Dimensions	Quantity	Dimensions
Electric charge.....	$[\epsilon]$	Inductance.....	$[L^2M\epsilon^{-2}]$
Current.....	$[T^{-1}\epsilon]$	Dielectric constant..	$[L^{-2}T^2M^{-1}\epsilon^2]$
Potential.....	$[L^2T^{-2}M\epsilon^{-1}]$	Magnetic pole.....	$[L^2T^{-1}M\epsilon^{-1}]$
Resistance.....	$[L^2T^{-1}M\epsilon^{-2}]$	Magnetic field.....	$[L^{-1}T^{-1}\epsilon]$
Conductance.....	$[L^{-2}TM^{-1}\epsilon^2]$	Permeability.....	$[LM\epsilon^{-2}]$
Capacity.....	$[L^{-2}T^2M^{-1}\epsilon^2]$		

The simplest and most obvious arbitrary definition for the unit charge is the elementary charge. This is, however, inconveniently small, and we may define the unit charge as being equal to the sum of  $1/4.774 \times 10^{-10}$  elementary charges in the electrostatic system,



or of  $3 \times 10^{10}/4.774 \times 10^{-10}$  in the electromagnetic system, without causing any internal disorder in our present c.g.s. system of units. The electrostatic and electromagnetic c.g.s. units are not, however, of convenient size for most of the usual laboratory measurements, and it has been found desirable to define a so-called "practical" system of units having a simple relation (powers of 10) to the c.g.s. units. This practical system includes the coulomb, ampere, volt, ohm, reciprocal ohm, etc.

Here again we have an illustration of the principles we have been discussing. If we limit ourselves to these five physical quantities, there are three relationships existing among them. It is necessary, therefore, to define the units of two quantities; the other three can be derived. The ohm and the coulomb are generally selected for definition. From the coulomb the ampere is derived, making use of the relationship connecting quantity of charge and strength of current with time. From the ohm and the ampere, using Ohm's law, the volt is derived; and from the ohm comes the reciprocal ohm. The student should construct a table showing the numerical relationship between each one of these practical units, and the corresponding electromagnetic and electrostatic units.

Many students experience difficulties in handling units, and indeed also in the use of equations, those symbolic representations of physical laws. The difficulty is frequently due to a failure to understand the basic meaning of units and equations. For example, to many students Ohm's law, the statement that "current is equal to potential divided by resistance," is about as full of meaning as the statement that double-stars are equal to barber-shops divided by guinea-hens. It is nonsense to equate such dissimilar things, and barber-shops cannot be intelligibly divided by guinea-hens, any more than electrical potential can be divided by electrical resistance. But Ohm's law does not mean what it seems to say. It should be stated primarily in the form

$$i = k \times \frac{e}{r}.$$

It is perfectly intelligible that the strength of an electric current flowing through a conductor should be *directly proportional* to the electrical potential forcing it through, and at the same time should be *inversely proportional* to the resistance of the conductor. Dis-



similar things may be proportional even if they cannot be equal. Ohm's law is then not only understandable but it is true, and it is true regardless of whatever units may be chosen for measuring the three quantities, although, of course, the numerical value of  $k$  depends on the choice of these units. Now, if units of two of the quantities be arbitrarily defined, the third unit may be chosen in such a way that the proportionality constant  $k$  becomes equal to 1. The equation then seems to take on the form of an equality, but it should still be regarded as a proportionality in which the constant is 1. The equation then means that the current strength, measured in its unit, is numerically equal to the potential, measured in its unit, divided by the resistance, measured in its unit.

Perhaps it is worth while to illustrate with a more homely example. To say that the growth of corn is *proportional* to rainfall is an intelligible statement, whether it is correct or not. But to say that the growth of corn is *equal* to rainfall is nonsense. If we measure the growth in a certain unit, say inches, it is possible, however, to choose a unit for measuring rainfall so that the growth will be numerically equal to the rainfall, that is, the proportionality constant will become 1. With this restricted meaning in mind, it is then no longer nonsense to equate the growth of corn and rainfall.

Let us now return to Table I, with its list of physical quantities, and their dimensions. Suppose that instead of taking length, time and mass for arbitrary definition of the fundamental units, we should take length, time and force. What then would be the dimensions of the quantities listed? The dimensions of the first seven, including acceleration, would of course be unaffected. The dimensions of mass would be  $[FT^2L^{-1}]$ , of force would be  $[F]$ , of energy  $[FL]$ , of power  $[FLT^{-1}]$ , of momentum  $[FT]$ , of pressure  $[FL^{-2}]$ , etc. The student should complete the list, and also work out all the dimensional formulas for Table I, assuming that length, time and *energy* units are made fundamental.

One of the most useful applications of dimensional reasoning is in testing the validity of equations. Every equation has a left-hand and a right-hand member, separated by an equality sign. While measurable quantities may occur on one side which are entirely different from those on the other side, the dimensions of all the terms on one side must reduce to the same dimensions as on the



other, if the equation is valid. In mathematical parlance, all equations expressing physical relationships are dimensionally homogeneous. Take, for example, the equation

$$s = 1/2 \, g t^2.$$

If this equation is valid, the terms on the right must reduce to dimensions of length, since  $s$  represents a distance.  $g$  represents the acceleration of the earth's gravitational field, and has the dimensions  $[L T^{-2}]$ . Then,  $[L T^{-2} \times T^2] = [L]$ . Therefore the equation is valid as far as sameness of dimensions is concerned. Of course, there may be other things wrong with it; the numeric (or dimensionless quantity)  $1/2$ , appearing on the right-hand side, may be incorrect. Dimensional reasoning tells us nothing about its correctness; we must resort to other methods, those of experimental science, to test its accuracy.

Let us take as another example the Clapeyron equation

$$\frac{dp}{dT} = \frac{L_v}{T(v_1 - v_2)}.$$

The dimensions on the left-hand side are those of pressure, namely  $[L^{-1} T^{-2} M]$ , divided by temperature, or  $[L^{-1} T^{-2} M \theta^{-1}]$ . On the right-hand side the dimensions of  $L_v$ , the latent heat of vaporization, are those of energy, namely,  $[L^2 T^{-2} M]$ . This divided by  $[L^3]$  (volume) gives  $[L^{-1} T^{-2} M]$ , the dimensions of pressure; and this divided by temperature gives  $[L^{-1} T^{-2} M \theta^{-1}]$ , the same dimensions as those appearing on the left-hand side, thus proving the validity of the equation, dimensionally. Again, let us consider the equation of Poiseuille

$$V = \frac{\pi p r^4 t}{8 l \eta}$$

where  $V$  represents the volume of liquid which flows,  $p$  represents the hydrostatic pressure,  $r$  the radius of the capillary tube,  $t$  the time,  $l$  the length of the tube and  $\eta$  the viscosity of the liquid. The dimensions on the left are  $[L^3]$ . On the right we have

$$[L^{-1} T^{-2} M \times L^4 \times T] \div [L \times L^{-1} T^{-1} M \text{ (viscosity)}] = [L^3],$$

the same as those on the left. Of course  $\pi$  is dimensionless.

There are other useful applications of dimensional reasoning. For example, it is often possible by using dimensional reasoning,



to discover the exact (and previously unknown) relationship existing among a set of variables, when all of the variables playing a part in the given effect are known. R. E. Wilson and D. P. Barnard, in an article "The Mechanism of Lubrication," *J. Ind. Eng. Chem.*, 14, 682 (1922), give a suitable illustration. It is known that the load pressure in a bearing is some function of viscosity (of the lubricant) and frequency of revolution,  $p = f(\eta, n)$ . Since the equation must be dimensionally homogeneous, and since the dimensions of pressure are  $[ML^{-1}T^{-2}]$ , of viscosity  $[ML^{-1}T^{-1}]$  and of frequency  $[T^{-1}]$ , it follows that  $p = k \cdot \eta \cdot n$ , for then we have  $[ML^{-1}T^{-2}] = [ML^{-1}T^{-1}][T^{-1}]$ . The constant  $k$  is dimensionless.

Starling, *Electricity and Magnetism*, p. 384, gives two further examples. The student should attempt to derive these equations by dimensional reasoning before looking up the reference: (1) The excess air pressure inside a soap bubble is some function of the surface tension and of the radius of the film. (2) The velocity of a compression wave, i.e. a sound wave, in a gas is some function of the pressure and density of the gas.

As a further exercise the student should prove the dimensional homogeneity of the following equations which are some of the common equations met with in a systematic course in physical chemistry.

$$f = \frac{d(mV)}{dt}, \quad \text{where } f \text{ represents force, } m \text{ mass, } V \text{ velocity, and } t \text{ time.}$$

$$p = nkT, \quad \text{where } p \text{ represents pressure, } n \text{ number of molecules per cc., } k \text{ is the Boltzmann gas constant, and } T \text{ temperature.}$$

$$u = \sqrt{\frac{3RT}{M}}$$

$$w/(a \cdot t) = p \sqrt{\frac{M}{2\pi RT}}, \quad \text{where } w \text{ represents mass, } a \text{ area, } t \text{ time, } p \text{ pressure, } M \text{ molecular weight (mass), } R \text{ the universal gas constant, and } T \text{ temperature.}$$

$$E_r = \frac{n(n+1)h^2}{8\pi^2 I}, \quad \text{where } E_r \text{ represents energy of molecular spin, } n \text{ is an integral number, } h \text{ is Planck's constant of action, and } I \text{ is moment of inertia.}$$



$\sigma = 1/2 r h d g$ , where  $\sigma$  is surface tension,  $r$  radius,  $h$  height,  $d$  density and  $g$  the acceleration of the earth's field.

$\sigma \left( \frac{M}{d} \right)^{\frac{2}{3}} = k(T_c - T - 6^\circ)$ , where the symbols have meanings already given above. What are the dimensions of  $k$ ? How should it be expressed in c.g.s. units?

$n\lambda = 2d \cdot \sin \theta$ , where  $n$  is an integral number,  $\lambda$  is wave-length,  $d$  is distance between planes in a crystal lattice, and  $\theta$  is an angle.

$$H = q_v + \Delta n \cdot RT$$

$\frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2} = \mathcal{R}$ . What are the dimensions of  $\mathcal{R}$ ?

$m = e \cdot l$ , where  $e$  is electric charge, and  $l$  is distance between  $+$  and  $-$  charges. What does  $m$  represent here?

$$E = E_0 - \frac{RT}{23,060 n} \ln K$$

$L = n_1 z_1 \mu_1 + n_2 z_2 \mu_2$ , where  $L$  is specific conductance (conductivity),  $n$  is no. of ions per cc.,  $z$  is valence, and  $\mu$  is mobility. (Conductivity has the dimensions  $L^{-2} T M^{-1} \epsilon^2$ .)

Enough discussion of dimensional reasoning as well as exercise in its uses has now been given to indicate the great clarification of thought which it brings. Any effort spent in the mastery of the fundamental principles of this reasoning will be many times repaid in the student's later mental development.

Many references might be cited in connection with the theory of units and dimensions, but only a few of the probably more available ones have been selected and are given here for the student to look up.

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## EXERCISE II

### ERRORS OF MEASUREMENT; ILLUSTRATED BY BAROMETER READINGS

In the measurement of physical quantities, no matter how carefully the measurements may be made, errors occur. Some of the typical errors, their estimation and expression, will be considered in the present exercise in connection with the measurement of atmospheric pressure with a barometer.

It is assumed that a barometer of the Fortin type is available. This barometer, hanging vertically on the laboratory wall, consists essentially of a glass tube about 90 cm. long which has been sealed at one end, filled with mercury, and "boiled out" to remove as far as possible all air and water vapor, and has then been inverted in a small cistern of mercury, thus permitting the mercury column to fall away some distance from the top of the tube to give a Torricellian vacuum. The height of the mercury column above the level of the mercury in the cistern is read on a brass scale provided with a vernier. As the height of the mercury column alters with changing atmospheric pressure, the level of the mercury in the cistern becomes changed slightly, and in order to make the reference level of the cistern always the same, an adjustment screw is provided by means of which a soft leather bag comprising the bottom of the cistern may be either compressed or allowed to expand. In this way the mercury surface can be brought to such a level that it just touches a fixed ivory fiducial pointer inside the cistern.

Take twenty successive readings of the barometer, each time resetting the cistern level on the ivory point and reading with the scale vernier to 0.1 mm., or if possible to 0.05 mm. Record the twenty values in Column I of a table now to be constructed. In Column II list the temperatures read off from the thermometer attached to the front of the barometer near the middle. It is good practice to read the thermometer first, and then the barometer, to avoid affecting the thermometer with heat from the



observer's body. These barometer readings are subject to a number of errors, the principal ones of which will now be discussed.

(1) In the first place, since the time required for completion of twenty readings will amount to at least 10–20 minutes, the atmospheric pressure itself may change considerably from first to last. If so, the fact will be indicated by the trend of the barometer readings, unless the actual change is so small as to fall within the error of measurement. The timing of the readings will naturally depend on the purpose for which they are needed. The necessity of knowing the pressure at some particular instant will call for one reading only. If the average pressure over a certain time is required, readings should be taken at regular intervals during this time. In the present exercise twenty successive measurements are made merely so that the average value may be obtained, and the properties of the average discussed. It is assumed that the barometric pressure remains constant during the entire interval.

(2) The readings may be subject to instrumental errors. Perhaps the barometer scale has not been properly constructed, so that the point on the scale marked 760 mm. is not actually 760 mm. distant from the tip of the ivory pointer in the cistern. This error might more appropriately be called a defect, since it is avoidable, and is due to improper construction. Instrumental errors of this sort are very common whenever a scale is involved, as, for example, in the use of voltmeters, ammeters, thermometers, refractometers, stop-watches, etc., and such errors are usually eliminated by careful calibration of the instrument either by comparison with a standard instrument or by locating a small number of "fixed points" on the scale, from which the rest of the scale can be evaluated.

Another instrumental error which enters into the barometer readings is that caused by the presence of a small quantity of gas above the mercury; that is to say, the Torricellian vacuum is not perfect. The gases usually present are air, water vapor and, of course, mercury vapor. The pressure of the latter increases with rising temperatures in a manner given approximately by the equation

$$p = 0.0002 t \text{ cm.,}$$



where  $t$  is expressed in degrees Centigrade. This correction must be added to the barometer reading. In the present exercise it will be assumed that both of these possible instrumental errors, that due to an imperfectly constructed scale and that due to an imperfect vacuum, are negligible.

There is a third instrumental error which should, however, be taken into consideration, namely, the capillary depression of the mercury in the barometer tube. The extent of this depression depends on the diameter of the tube and also on the angle of contact which the mercury makes with the glass. The size of this angle is indicated roughly by the shape of the meniscus. If the meniscus is comparatively flat, the error is small, but if well-rounded and high, the error is larger. The shape of the meniscus depends on a number of factors such as the presence of gases in the Torricellian vacuum, the presence of minute traces of metallic impurities in the mercury, the manner in which the glass tube was originally cleaned, etc. The following table (taken from the *Kaye and Laby Tables*) indicates the size of the correction (mm.) to be added to the barometer readings.

TABLE IV

Bore of tube, mm.	Height of meniscus in mm.							
	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
6	.27	.41	.56	.78	.98	1.21	1.43	
7	.18	.28	.40	.53	.67	.82	.97	1.13
8	...	.20	.29	.38	.46	.56	.65	.77
9	...	...	.21	.28	.33	.40	.46	.52
10	...	...	.15	.20	.25	.29	.33	.37
11	...	...	.10	.14	.18	.21	.24	.27
12	...	...	.07	.10	.13	.15	.18	.19

If the diameter of the tube is larger than 2–2.5 cm. the capillary correction is negligible. Sometimes the scale is constructed so that the capillary correction is made automatically. Unless a specific statement that this is the case accompanies the barometer, correct the twenty barometer readings for capillarity and enter the corrected values in Column III. The error due to the capillarity



is not, except in the case of large bore glass tubes, an avoidable error. It is inherent in the very structure of the instrument.

(3) Since the density of the mercury becomes less with rising temperature, the height of the mercury column required to balance the atmospheric pressure increases. For this reason it is customary to calculate the height which the mercury column would have at a standard temperature, namely,  $0^{\circ}\text{C}$ . If  $\alpha$  is the coefficient of cubical expansion of mercury, then  $h_0$ , the height at  $0^{\circ}$ , is given by the equation

$$h_0 = h_t / (1 + \alpha t)$$

where  $h_t$  is the observed height and  $t$  is the observed temperature (Centigrade). This becomes, on performing the division,

$$h_0 = h_t(1 - \alpha t)$$

if terms involving  $\alpha$  raised to greater than the first power are neglected. The length of the brass scale also increases with rising temperature, and since a lengthening of the scale has the effect of making the height of the mercury column appear too small, the combined correction for the effect of temperature on the mercury and on the scale is

$$h_0 = h_t(1 - \alpha t)(1 + \beta t)$$

where  $\beta$  is the coefficient of linear expansion of brass. This equation reduces to the form

$$h_0 = h_t[1 - (\alpha - \beta)t - \alpha\beta t^2]$$

and if the very small term  $\alpha\beta t^2$  is neglected and the numerical values of  $\alpha$  and  $\beta$ , namely 0.000184 and 0.000020, are substituted we obtain

$$h_0 = h_t(1 - 0.000164 t).$$

Correct the barometric readings listed in Column III of the table for the temperature effect on both the mercury and the brass scale and record the corrected values in Column IV.

(4) Since the value of  $g$ , the acceleration of the earth's gravitational field, varies with altitude, that is with distance from the earth's center, and also since it varies with latitude because of the spheroidal shape of the earth, it is the convention to define the standard  $g$  as that which is found at sea-level at latitude  $45^{\circ}$ .



Suppose that the barometer is situated in latitude  $\lambda$  and at an altitude of  $l$  meters above sea-level, then the height of the barometric mercury column which would be observed in a standard gravitational field may be calculated by multiplying the actually observed height by

$$(1 - 0.0026 \cos 2 \lambda - 0.0000002 l).$$

This is the correction when the latitude  $\lambda$  is south of  $45^\circ$ ; when it is north of  $45^\circ$ , the correction  $0.0026 \cos 2 \lambda$  is plus instead of minus.

If the combined correction for altitude and latitude amounts to 0.05 mm. or more in the case of the barometer involved in this exercise, make the correction for the twenty barometer readings of Column IV, and place the corrected values in Column V.

The errors introduced into the barometer readings because of the temperature, altitude and latitude, are due to the conditions of the environment in which the instrument happens to be located, and they are for that reason often referred to as "condition errors." Such errors are very common with instruments of all sorts.

(5) All of the errors mentioned thus far, both those belonging to the instrumental type and those of the condition type, are often classified as constant or systematic errors. Such errors nearly always occur, unless some special means are taken for their elimination. These errors cannot be eliminated by merely repeating the measurements, no matter how often the repetition may be made. It is one of the principal objectives, and one of the objectives most difficult to attain, in the science of measurement to eliminate or allow for such constant errors. But even after every allowance for constant errors has been made, as far as possible, as, for example, has been done with the barometric readings in Column V, there are still variations among the different results. It is difficult if not impossible to account for the occurrence of such variations. They seem simply to happen, and are for that reason usually spoken of as chance errors, erratic errors, or accidental errors.

The problem which now confronts the observer is to select from the twenty barometric readings of Column V the value which corresponds to the actual barometric pressure. It is naturally impos-



sible to obtain the exact value for the pressure; all that can be done is to obtain the best representative value, the value which is probably most nearly right, and to obtain the extent to which this value may probably deviate from the actual value. The arithmetic mean of the results is coming to be more and more regarded with favor as the best or most probable value, at least in chemical work. It is indeed seldom that chemists have occasion to make measurements of a sufficiently high order of accuracy to justify any more elaborate treatment of the results than that of finding the arithmetic mean.

**The Arithmetic Mean.** Calculate the arithmetic mean of the twenty barometric readings in Column V. Now, find the deviation of each separate reading from the mean, and regardless of whether these deviations are plus or minus, add them all together and divide by 20 to obtain the average deviation of a single reading from the mean. Divide the average deviation of a single observation by  $\sqrt{20}$  to obtain the average deviation or error of the mean value. It is a very satisfactory practice to express most types of experimental results in the form of the arithmetic mean plus or minus the average error of the mean. In symbolic form, the average error  $a$  of a single observation is given by the equation

$$a = \pm \frac{\Sigma d}{n}$$

where  $\Sigma d$  denotes the sum of all the deviations, regardless of sign, and  $n$  is the number of observations. The average error,  $A$ , of the mean is given by

$$A = \pm \frac{\Sigma d}{n\sqrt{n}}.$$

Derivation of the last equation is beyond the scope of this exercise. For its derivation as well as that of the following relationships, the student is referred to Chapter IX of Mellor's *Higher Mathematics for Students of Chemistry and Physics*.

**Probable Error.** If the deviations are arranged in a series in the order of their magnitude, that value for the deviation which is situated midway between the extremes, so that there are as many deviations smaller than this value as there are larger, is called the probable error. "Probable" here means simply a 50-50 chance that the number of errors smaller than this assumed



value is the same as the number of errors which are larger; it does not mean that the probable error is the one which is most likely to occur, nor does it mean that it is the most likely value for the actual error. It can be shown that  $r$ , the probable error of a single observation, is given by the equation

$$r = \pm 0.675 \sqrt{\frac{\Sigma(d^2)}{n-1}}$$

and that

$$R = \pm 0.6745 \sqrt{\frac{\Sigma(d^2)}{n(n-1)}}$$

where  $R$  is the probable error of the arithmetic mean. This is equivalent to writing

$$R = \pm \frac{r}{\sqrt{n}}.$$

Calculate  $r$  and  $R$  from the twenty barometric readings.

**The Mean Error.** A method frequently employed to express the error is that of the "mean error," or the standard deviation, or the mean-square deviation, or the root-mean-square deviation, as it is variously called. This is "the error whose square is the mean of the squares of all the errors; or the error which, if it alone were assumed in all the observations indifferently, would give the same sum of the squares of the errors as that which actually exists." (See Mellor, Chapter IX.) Hence,

$$m = \pm \sqrt{\frac{\Sigma(d^2)}{n-1}}$$

and

$$M = \pm \sqrt{\frac{\Sigma(d^2)}{n(n-1)}}$$

where  $m$  and  $M$  represent the mean errors which affect respectively a single observation and the arithmetic mean of all the observations.

Calculate  $m$  and  $M$  from the twenty barometric readings, and compare the values with  $a$  and  $A$ , and  $r$  and  $R$  above. Any one of these different methods may be taken as giving the degree of precision of a single observation as well as of the mean of all the observations, but it should be remembered that a high degree of precision does not necessarily imply a high degree of accuracy, since the results may be vitiated by constant or systematic errors.



For a discussion of the theory and method of least squares, the student is referred to some of the special treatises on this subject (e.g., see Mellor, Chapter IX).

**Propagation of Errors.** If  $B$  represents a measured value and  $e$  its error, then if  $B_1 \pm e_1$  is added to or subtracted from  $B_2 \pm e_2$ , the possible error may be as large as  $\pm(e_1 + e_2)$ .

In multiplication and division, if  $e_1$  and  $e_2$  are small compared with  $B_1$  and  $B_2$ , then the possible error is  $\pm(B_1e_2 + B_2e_1)$ . The possible *percentage* error of a product or a quotient is equal to the sum of the percentage errors of the factors involved.

If  $B_1 \pm r_1$ , where  $r_1$  represents the probable error, is added to or subtracted from  $B_2 \pm r_2$ , the probable error of the sum or difference can be shown to be equal to  $\pm\sqrt{r_1^2 + r_2^2}$ .

Similarly, in multiplication, the probable error of the product or quotient is equal to  $\pm\sqrt{(B_1r_2)^2 + (B_2r_1)^2}$ , and the probable error of the quotient  $B_1/B_2$  is equal to  $\pm\sqrt{\frac{(B_1r_2)^2}{B_2^2} + r_1^2}/B_2$ .

If  $(B \pm r)$  is raised to a power  $n$ , then the probable relative error of the final result is equal to  $n \times \frac{r}{B}$ , where  $\frac{r}{B}$  is the probable relative error of the original measurement.

An experimenter should, of course, make every effort to employ sound experimental technique, and to be sure that his results are trustworthy. It is essential for one who would become a proficient observer, to cultivate an attitude of indifference toward the results of his observations. All bias and desire for a certain experimental outcome should be suppressed. One's intellectual integrity is sometimes severely tested by the question of whether or not a particular result should be rejected, when the result diverges considerably from the average. Frequently there is an obvious and adequate reason for such rejection, but the mere fact of considerable divergence should not be allowed to influence the decision. A comment by Tuttle in his *Theory of Measurements* is very much to the point. "The temptation, often felt by the beginner, to omit or re-determine a discordant result may be very perceptible . . . A re-determination is not intrinsically objectionable, but it should be made *in addition* to the other determination, not *in place* of it."

Acc. 20476



**Significant Figures.** It is a very common mistake to express an experimental result, or a result calculated from experimental data, *with too many significant figures*. Let us take an example. Suppose that a volume of chloroform, in a suitable volume-meter, such as a burette or a pipette, is found to be 20 cc. at 15° C., and then is found to have a mass of 29.9807 g. If the mass is divided by the volume and the division is continued until there is no remainder, we obtain 1.499035 as the density of chloroform. It is absurd to state the density in this way, as it would indicate that the density had been determined to the 6th decimal place, or with an accuracy of about 1 in 1.5 million parts. While it is experimentally possible with extreme precautions to weigh such a quantity of *chloroform* to the 4th decimal place, or with an error of only about 1 in 300,000 parts, it would be a difficult task. With good temperature control and proper technique one could measure a volume of 20.00 cc. to the 2nd, and with some difficulty to the 3rd decimal place, if the purity of the chloroform justified the attempt. But to expect to do so with an accuracy of 1 in 1.5 million parts would be ridiculous.

Furthermore, all considerations of experimental possibilities aside, when the volume of the chloroform is stated as being 20.0 cc. as above, it is understood that this means that the accuracy of the volume measurement is no greater than 1 in 200 parts. The calculated density can therefore have no greater accuracy than this, no matter how exactly the mass may be determined, and the figure 1.499035 should be changed to 1.499 or, better, rounded off to 1.50. If a slide-rule were used for this calculation, the number 29.9807 could not be located more accurately than to 4 or 5 in the second decimal place, and hence the result would automatically contain about the right number of significant figures. This is one of the general advantages of using a slide-rule.

The accuracy with which the least accurately determinable physical quantity can be measured should be allowed to control the accuracy with which the observer attempts to measure the other factors involved. If in the case of the density of chloroform the volume is not determined more accurately than 1 in 200 parts, it is needless to try to measure the mass much more accurately than this. Such accuracy would be superfluous. But if a measured quantity enters into an equation as a term raised to a power



greater than one, then it should be determined with correspondingly more accuracy. The propagation into a final calculated result of errors present in the data has just been considered in the preceding section.

It is important in the expression and calculation of results for the student to keep constantly in mind this matter of significant figures. A satisfactory rule to follow in the calculation of results from data is as follows: *In addition and subtraction, drop every digit in the final result which falls under an unknown digit in any of the quantities to be added or subtracted; and in multiplication and division, the final result should retain only as many significant figures as there are in the term or factor containing the smallest number of significant figures.*



### EXERCISE III

#### FUNCTIONAL RELATIONSHIPS; LAW OF DECAY; BOLTZMANN FACTOR

For the student of physical chemistry there is probably nothing more important in his mental development than the acquirement of good appreciation of the meaning of a "functional relationship." Most students entering upon a study of physical chemistry have been put through courses in college algebra, trigonometry, analytical geometry and calculus; and most of them have attained some little proficiency in performing the simpler algebraic operations of differentiation and integration. But it is seldom that a student is found to have developed any appreciable skill in expressing a physical relationship in the form of a graph and especially in the form of an equation, or developed much ability to read a physical meaning into the mathematical symbols and equations which he encounters in his text-books and in his readings in the literature.

The two preceding exercises, *Units and Dimensions* and *Errors of Measurement*, have been put into this manual with the hope that they might help the student in his effort to employ the language of mathematics in the description and discussion of physical and chemical effects. The present exercise is also designed to help in this effort. It is an illustration of one of the most common forms of the "scientific method" of approach to a technical problem.

In this particular form of the scientific method the logic involves four distinct steps. (1) The investigator, who is interested in some problem, first of all dreams about it, and if he possesses a sufficiently good imagination he finally is able to reach down into his physical and chemical background of fact and analogy and bring forth a "hunch" or hypothesis regarding the possible mechanism or nature of the effect in which he is interested. (2) This hypothesis is then expressed in the form of a differential equation. (3) The differential equation is integrated. (4) Data



obtained by an experimental study of the problem in the laboratory are then substituted into the integrated equation to test the equation's validity. If the equation holds, that is, if it really adequately describes the effect in question, there is good reason for believing that the original hypothesis is correct. This equation may then also be used for making quantitative predictions. The student should realize that the ability to *predict* is one of the most important characteristics of the "scientific method."

To illustrate these various points we may now proceed to the consideration of a simple technical problem. We shall choose for our "functional relationship" an example of the so-called "law of decay." Suppose that we have a large vertical cylindrical tank of uniform cross-section, and filled with liquid, such as a water-tower, and that the liquid is running out of an exit orifice at the bottom of the tank. Suppose that we would like to know whether or not there is any relationship between the rate at which the liquid escapes and the quantity of liquid in the tank.

(1) A plausible hypothesis which comes to mind almost at once is the guess that the rate of escape is directly proportional to the hydrostatic pressure, and hence also directly proportional to the volume of liquid in the tank. This is the first step: our hypothesis has been set up.

(2) To express this hypothesis in the form of a differential equation, let us allow the symbols  $V$  and  $t$  to represent volume and time, then

$$-\frac{dV}{dt} = k \cdot V, \quad (1)$$

where  $k$  is a proportionality constant. Here we have said with shorthand mathematical symbols exactly what we have already said in words, in the statement of our hypothesis. The differential quotient  $\frac{dV}{dt}$  stands for the rate of escape of the liquid, since it represents the rate of change of volume with time. The symbols of the differential calculus are needed, of course, because the rate is not a constant one, but itself changes with time. The minus sign indicates that the volume,  $V$ , in the tank is not increasing as time goes on, but decreasing.

(3) Now let us integrate; that is, let us add up by the methods of the integral calculus enough of the infinitesimals  $dV$  and  $dt$  to



give us finite and large enough quantities of  $V$  and  $t$  to deal with conveniently in our laboratory measurements.

$$-\int \frac{dV}{V} = k \int dt.$$

Upon integration (without limits), we have

$$\ln V = -kt + C$$

and, evaluating the integration constant  $C$ ,

$$\ln \frac{V}{V_0} = -k \cdot t \quad (2)$$

where  $V_0$  is the volume of the liquid in the tank when  $t = 0$ , namely at the beginning, when the flow first starts. Using logarithms to the base 10 instead of the base  $e$ , we get

$$2.303 \log \frac{V}{V_0} = -k \cdot t. \quad (3)$$

Both Equations 2 and 3, above, may be changed from the logarithmic to the exponential form, thus

$$\frac{V}{V_0} = e^{-kt} \quad (4); \quad \text{and} \quad \frac{V}{V_0} = 10^{-kt/2.303}. \quad (5)$$

The Equations 2, 3, 4, 5 are all different forms of the same functional relationship, and they all mean the same thing. Any one of them may be selected for use in the treatment of the experimental data to be collected in the fourth step, below; but it is most convenient to use Equation 3. This can be put into still more convenient form by getting rid of the minus sign, and this can be done without changing the meaning of the equation in any way, of course, by inverting the ratio  $V/V_0$  at the same time that we change the  $-$  to  $+$ . Thus,

$$2.303 \log \frac{V_0}{V} = k \cdot t. \quad (6)$$

(4) To make the actual measurements we may use a burette, which is a miniature tank. The stop-cock C from a 50 cc. burette should be cut off and sealed into the side of the burette B opposite the last graduation mark, as shown in Fig. 1. Some burettes are scaled from 0 to 50 cc., and others from 50 to 0 cc. But this



arrangement is immaterial since in either case the volume of liquid remaining in the burette can be easily determined. The exit tip of the stop-cock should be drawn out in a flame to a fine capillary and cut off to a length of a few centimeters. Then by manipulating the cock, a convenient rate of liquid flow, say 5 or 10 cc. for the first minute, can be produced. Once this suitable

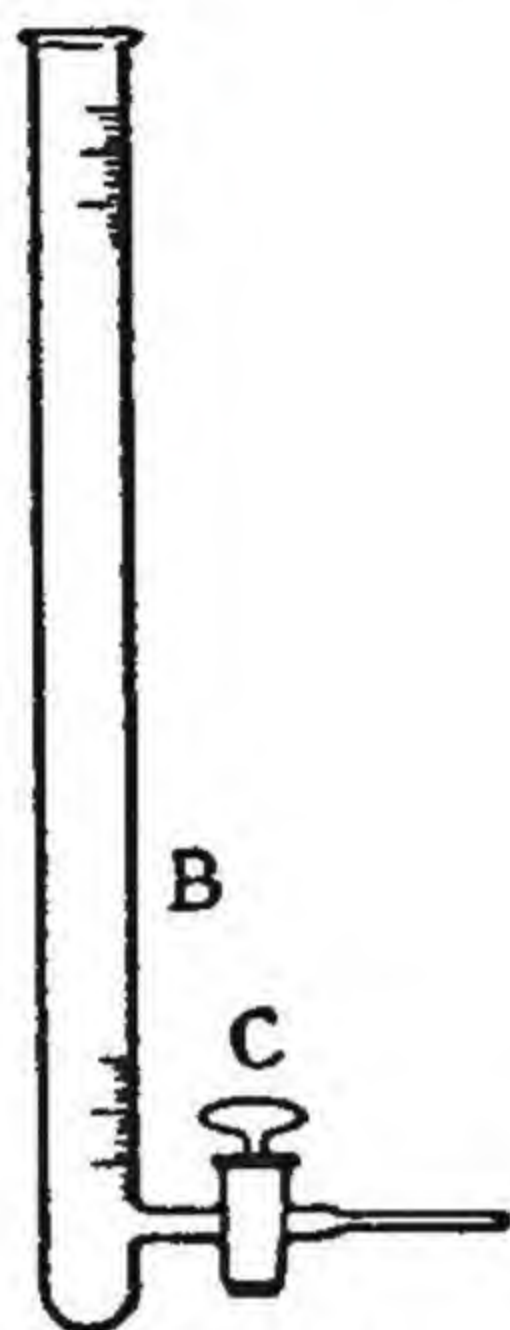


FIG. 1

setting of the stop-cock has been determined by a little experimentation, it should not be further disturbed, but kept exactly the same throughout the course of the measurements.

Fill the burette to a point above the scale with some liquid. Water, which has been colored by the addition of a small bit of dye to improve the visibility, is very satisfactory. As the meniscus passes the first scale mark, start a stop-watch; and at regular intervals, either half-minutes or minutes, read the volume of water left in the burette, until the burette is drained practically to the level of the stop-cock. Make up a table of data, listing time intervals in the

first column, corresponding values of  $V$  in the second column, ratios of  $V_0/V$  in the third column, and in the fourth column list the values of  $k$  calculated from Equation 6.

The test of the validity of Equation 6 is *the constancy of  $k$* . The principal errors which may enter into these measurements are: (a) the error introduced by the difficulty of reading the position of the moving meniscus to much better than 0.1 cc. at a definite instant of time; (b) the error introduced by the departure of the burette from perfectly uniform cross-section from top to bottom; (c) the error introduced because of the fact that the surface tension of the last drop of water to escape prevents the water in the burette from actually falling to the level of the stop-cock. Thus  $V_0$  instead of being exactly 50, is something less than 50. Correction can of course be made, and the true head of water in terms of volume ( $V_0$ ) for zero time can be calculated, and used instead of 50 cc. None of these errors are generally serious. This experiment if properly performed gives excellent values for  $k$ .

Plot the different volumes of water in the burette on an ordinate



axis against the respective time intervals on the abscissa axis. What is the significance of the intercept on the volume axis in such a plot? What is the physical meaning of tangents drawn to the curve at various points along its length?

Now, plot  $2.3 \log (V_0/V)$  against  $t$ . What is the meaning of the slope in this plot?

Calculate the average value for  $k$ , and the mean deviation from the average. (See Exercise II.) Using this average value of  $k$  in Equation 6, calculate the "half-life" time, i.e. the time required for half of the water to run out of the burette, and insert this *interpolated* value in your table, above. Calculate the time required for 25% of the water to escape. Predict what volume of water runs out during the 75 seconds immediately following the end of the 5th minute, by first calculating the volume remaining in the burette at the end of 5 minutes, and then using Equation 1 *integrated between limits*.

$$\ln V_1 - \ln V_2 = k(t_2 - t_1)$$

If the student does not already appreciate the significance of "e," the base of the natural system of logarithms, he should consult Mellor's *Higher Mathematics for Students of Physics and Chemistry*, pp. 56-64, or Daniels' *Mathematical Preparations for Physical Chemistry*, pp. 126-141. There are many examples of the "law of decay" among common physical and chemical effects. In order that the student may derive as much benefit as possible from his experience in handling this type of mathematical technique, it is suggested that he investigate one of the effects mentioned below. No detailed directions will be given. The student is left to his own resources and ingenuity in planning the experimental work. The particular problem selected by the student will doubtless depend on the apparatus and equipment available.

(A) If the student can obtain a small tube of radon (radium emanation), such as is used in hospitals for treatment of cancer, the rate of decay may be studied over a period of a few weeks, with a large-leaf electroscope which is not too sensitive. The hypothesis would be that the rate of disintegration or decay is directly proportional to the quantity of the radio-active material.



The differential equation would be:

$$-\frac{dN}{dt} = k \cdot N$$

where  $N$  is the number of radio-active atoms present at any time  $t$ .

(B) If data regarding the atmospheric pressures at various altitudes above sea-level are available in some handbook or other source of information, the hypothesis that the rate of decrease of pressure,  $p$ , with increasing altitude,  $h$ , is directly proportional to the pressure, as expressed in the equation

$$-\frac{dp}{dh} = k \cdot p,$$

may be investigated.

(C) A solution of hydrogen peroxide, upon addition of a suitable catalyst, such as potassium iodide, can be made to decompose at a conveniently measurable rate. Thus the hypothesis that the rate of this chemical reaction is directly proportional to the concentration may be tested.

$$-\frac{dx}{dt} = k \cdot x.$$

(D) Is it true that when a beam of monochromatic light enters an absorbing medium the rate of fall-off in the intensity of the light with depth of penetration is directly proportional to the intensity of the light?

$$-\frac{dI}{dl} = k \cdot I.$$

A satisfactory source of light is a stereoptican lantern, or an electric light bulb and a suitable lens system to make the beam of one non-divergent and non-convergent, but parallel rays. A convenient arrangement is a vertical colorimeter tube (flat-bottomed), which may be filled to various measured depths with a colored dye solution, through which the beam of light is allowed to pass. The light may be made practically monochromatic by preliminary passage through a relatively thin layer of the dye solution. The intensity of the transmitted light in each case is measured relative to that of this incident monochromatic beam ( $I_0$ ). The intensity may be measured with a purchased or home-made thermopile



(connected to a sensitive galvanometer) or with a Crooks radiometer (assuming that the number of revolutions produced per minute is a measure of the light intensity).

### THE BOLTZMANN FACTOR

One of the most powerful mathematical tools available to the physical chemist in the interpretation of his experimental results, and in the prediction of new results, is the so-called "Boltzmann factor." Since this expression can be simply and easily derived from the argument which has already been developed in this chapter we shall now present it, and later in the manual we shall use it, or refer to it, in quite a number of different situations. It is important that the student, if he has an inferiority complex in connection with his mathematical prowess, get rid of such a complex at once. Certainly no more than average intelligence is needed to master the simple mathematical techniques that we are dealing with here. It is generally true that after one becomes accustomed to the use of symbols and learns the meaning of the particular set of conventional symbols employed for dealing with the phenomena of a certain field, most of the difficulties vanish; that is to say, the actual logical processes are generally relatively simple.

It has already been suggested to the student, in one of the foregoing exercises, that he integrate the equation

$$-\frac{dp}{dh} = k \cdot p \quad (7)$$

and by seeking in a handbook for data on the dependence of atmospheric pressure on altitude, test the validity of the equation. The integrated equation is actually found to hold extremely well,

$$\ln \frac{p}{p_0} = -kh \quad \text{or} \quad \frac{p}{p_0} = e^{-kh}$$

Now, with this much established, let us proceed as follows: Imagine a vertical column of air, 1 sq. cm. in cross-section, reaching from sea-level to the top of the atmosphere, as in Fig. 2. On any horizontal plane  $pl_1$  the pressure is the downward force (per sq. cm.) exerted by the weight of the whole column of the atmosphere. At a level 1 cm. higher, or  $\Delta h$  higher up, the pressure is less by the



amount  $\Delta p = m \cdot g$ , where  $m$  is the mass of the air in the cubic centimeter between the two planes  $pl_1$  and  $pl_2$ , and  $g$  is the acceleration of gravity. Thus

$$-\frac{\Delta p}{\Delta h} = m \cdot g.$$

If we wish to express the rate of variation of pressure with height as a function of air density, we shall have to do it in terms of  $\frac{\Delta p}{\Delta h}$  as  $\Delta h$  approaches zero, because the density itself falls off with increasing height. The exact expression, then, is

$$-\frac{dp}{dh} = \rho \cdot g \quad (8)$$

where  $\rho$  is density at any height  $h$ . Furthermore, since density is directly proportional to pressure (temperature being constant), it follows that

$$\frac{\rho}{\rho_0} = \frac{p}{p_0}$$

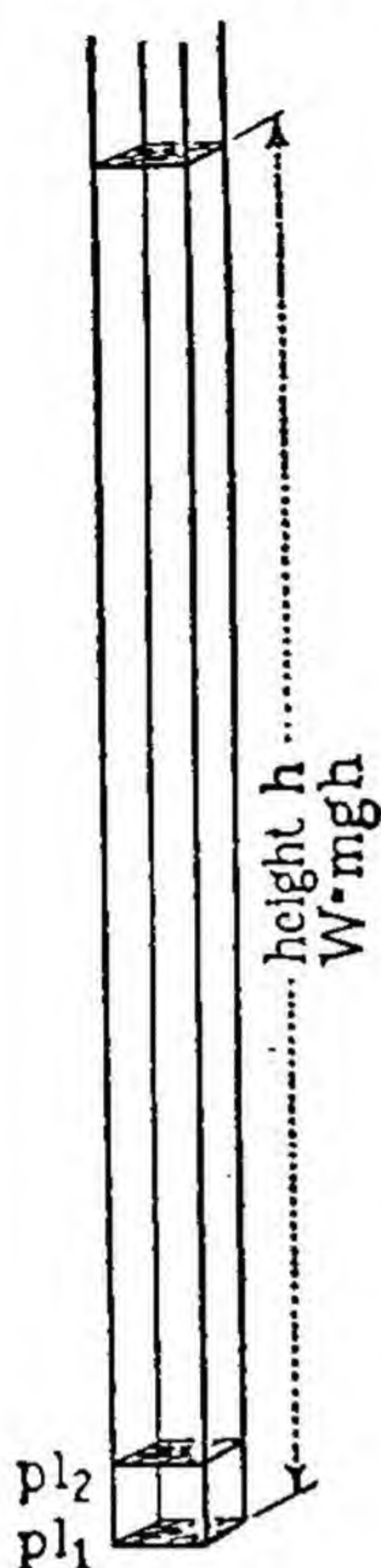


FIG. 2

where  $\rho$  and  $p$  are the density and pressure at any height  $h$ , and  $\rho_0$  and  $p_0$  are the density and pressure at sea-level. Therefore

$$\rho = \frac{\rho_0}{p_0} \cdot p$$

and substituting this value of  $\rho$  into Equation 8, we get

$$-\frac{dp}{dh} = \frac{\rho_0}{p_0} g \cdot p. \quad (9)$$

In other words  $k$  of Equation 7 is equal to  $\frac{\rho_0}{p_0} g$ . Integrating Equation 9 we get

$$\frac{p}{p_0} = e^{-\frac{\rho_0}{p_0} g \cdot h}. \quad (10)$$

Now, without destroying the validity of this equation we shall change its form in two ways. (1) Since the number of air molecules present per cc. is directly proportional to the pressure we



can write  $n/n_0 = p/p_0$ , where  $n$  and  $n_0$  are the numbers of molecules present per cc. at height  $h$  and at sea-level, respectively. (2) The density  $\rho_0$  is the mass per cc. at sea-level. If we multiply it by the number of cc. in a gram molecular volume at the prevailing temperature and pressure we get  $\rho_0 V = M$ , the molecular weight. At the same time we must multiply  $p_0$  in the denominator of the exponent by this same volume and we get

$$e^{-\frac{\rho_0}{p_0} g \cdot h} = e^{-\frac{\rho_0 V}{p_0 V} g \cdot h} = e^{-\frac{M g h}{R T}} = e^{-\frac{W}{R T}}$$

where  $R$  is the gas constant,  $T$  is the absolute temperature, and  $W$  is the work (namely  $Mgh$ ) which would be done in lifting a mol weight  $M$  of air from sea-level to any height  $h$ , against the downward pull of gravity. This expression  $e^{-W/RT}$  is the Boltzmann factor for the present situation. It may also be stated in the equivalent form,  $e^{-w/kT}$ , where  $k$  is the Boltzmann gas constant for one molecule (i.e.  $R \div 6.06 \times 10^{23}$ ), and  $w$  is the work of lifting one single molecule from the lower to the higher level. The Boltzmann factor gives the relative probability of finding molecules in two different energy states (in this case potential energy states in the earth's gravitational field), or it gives the relative population of molecules in two different energy states, because from Equation 10, it follows now that

$$\frac{n}{n_0} = e^{-\frac{w}{kT}} = e^{-\frac{W}{RT}}.$$

This relationship holds generally for any kind of a force field. If we know the work  $W$  required to change a mol from one energy state to another, or the work  $w$  required to change a single molecule from one energy state to another, we can calculate by means of the Boltzmann factor the relative numbers of molecules existing on the average in the two states. The surprisingly extensive applicability and usefulness of this functional relationship will be illustrated or referred to later in Experiments 4, 8, 12, 22, 25, 26, 29, 33 and 38.

#### REFERENCES:

- Mellor, *Higher Mathematics for Students of Chemistry and Physics*.  
 Daniels, *Mathematical Preparation for Physical Chemistry*.  
 Thompson, *Calculus Made Easy*.



## EXERCISE IV

### GLASS-BLOWING

The ability to construct glass apparatus, and to repair broken glassware is of inestimable value to the physical chemist. In the present exercise the simple operations of glass manipulation are performed by the student, and when these have been mastered a fairly complicated job of glass-blowing is assigned (Experiment 6).

If both soft sodium glass and pyrex glass are available, the student should practice making simple seals and "T"-tubes with both of them in order to observe the differences in their behaviour, and to learn how to work successfully with both of them.

**Necessary Equipment.** A good blast lamp is necessary, a source of compressed air, and of oxygen. An air-gas flame is not hot enough to make pyrex workable, and a mixture of air and oxygen is better than air alone for large pieces of soft glass. A sharp triangular file, or a glass-cutter's file (ordinary small flat file with the sides ground smooth), and a tapered piece of carbon rod (an arc-light carbon) complete the list of necessary tools. The carbon may be replaced by a flanging tool, consisting of a pointed triangular brass spatula two or three inches long mounted on a suitable handle. An assortment of small corks and a yard of quarter-inch P.G. flexible rubber tubing should also be available, and new wire gauze, matches, etc.

**Fundamental Operations. Cutting.** With the edge of the file make a scratch about an eighth of the way around the piece at the point where it is to be broken. Wrap the fingers about the piece so that the palms are down, and the index fingers side by side. The scratch is held towards you, opposite the point of contact of the index fingers, Fig. 3, and each thumb is pressed against the glass about half an inch beyond the scratch. The piece is now bent inward, which breaks it at the scratch, and pulled apart simultaneously, which insures a clean break. Moistening the scratch with the tongue seems to help.

Short ends cannot be broken off, or very large tubes broken



by this method. These are broken by means of heat expansion. The preliminary scratch is made as before, and moistened slightly, and a small bead of molten glass (end of a rod or tube) is pressed upon it. A complete break will result, or a crack that will permit the pieces to be pulled apart. Another method of breaking involves wrapping an electrically heated nichrome wire around the tube (particularly a large tube) at the point of the scratch.

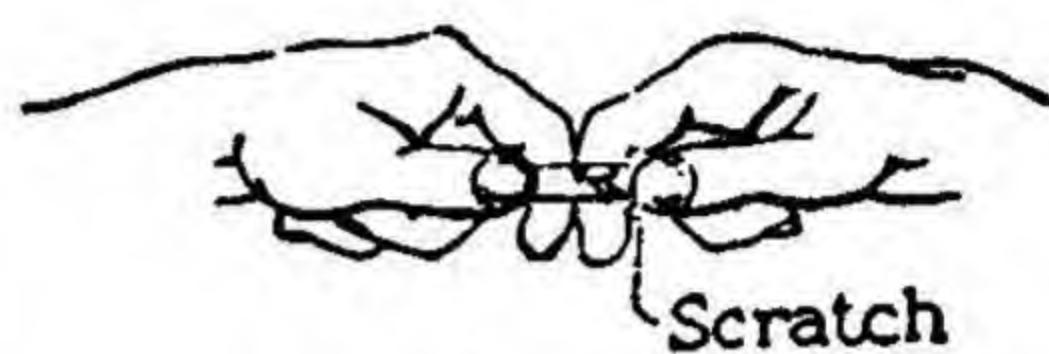


FIG. 3

**Straight Seals.** Select a piece of straight tubing. Break it as explained above, and then seal the broken ends together. If the break has not been clean, chip off any irregular pieces of glass with a wire gauze until the ends are squared. Hold a piece in each hand and bring both ends, to be sealed, into the flame together, having previously stopped up a far end of one of the tubes with a cork. (The instructor should give directions for regulating the flame properly.) Rotate both pieces so that the broken ends are heated uniformly. Bring the softened ends squarely into contact as soon as the glass has begun to glow, and before it has flowed appreciably. Be careful to press the pieces together so that no holes remain. Now rotate the tube until the weld is thoroughly soft, and remove it from the flame. Blow gently, through the open end, or through a flexible rubber tubing attached to the open end, until a uniform bulge appears, and then pull the pieces slightly apart until the bulge disappears. If one portion of the wall is thicker than the rest, this must be heated separately and blown out slightly. A good seal shows no marks of the original weld, and possesses walls of uniform thickness and as near as possible like the original tubing. *Anneal the weld* by allowing it to cool slowly in a smoky flame until carbon deposits on it.

Select two pieces of tubing of different diameter (say  $1/4''$  and  $1''$ ). The large tube must be reduced to the diameter of the small one. Stick a small piece of tubing to the edges of the large tube, at one end, to use for a handle. Now rotate the large tube in a hot flame and melt off the last inch or so, permitting the walls to collapse so that a large test tube is formed. Alternately heat and blow the end of this test tube until it is well rounded and of uniform thickness. Now with a hot pointed flame heat a spot



about  $3/8''$  in diameter at the very bottom of the rounded end, and blow out a *small* bubble. Then heat the bubble strongly and blow hard, and scrape off the balloon of thin glass. This will provide a round hole of suitable diameter for sealing on the smaller tube. The actual sealing operation is the same as with tubes of the same size, except that it will nearly always be necessary to flange the end of the smaller tube so that it fits exactly upon the hole prepared in the larger one.

**T-tubes.** Blow a small bubble on the side of a piece of tubing, and seal a flanged tube of suitable size onto this opening, using the same method as above. Be careful to eliminate any thickened portions around the seal by alternately heating and blowing. In order to facilitate blowing and to provide an air tight system it is generally advisable to seal up the outer ends of all small pieces of tubing that are to be sealed together, and to provide corks for the larger ones, with one opening left to blow through. After the actual blowing is completed the sealed off ends can be cut off and the broken places polished.

The student may experience the difficulty of having his glass crack while cooling. This will not occur if the glass is annealed by heating it thoroughly at the end of the operation, to remove strain, and further annealing it by letting it cool slowly (shut the air supply off gradually). Soft glass will be much harder to work with in this respect than pyrex, but the latter must also be treated carefully in the following procedure.

**Inner Seal.** Prepare a large piece of tubing as if to seal a small one to it, i.e., close one end, but do not blow a hole in the end.

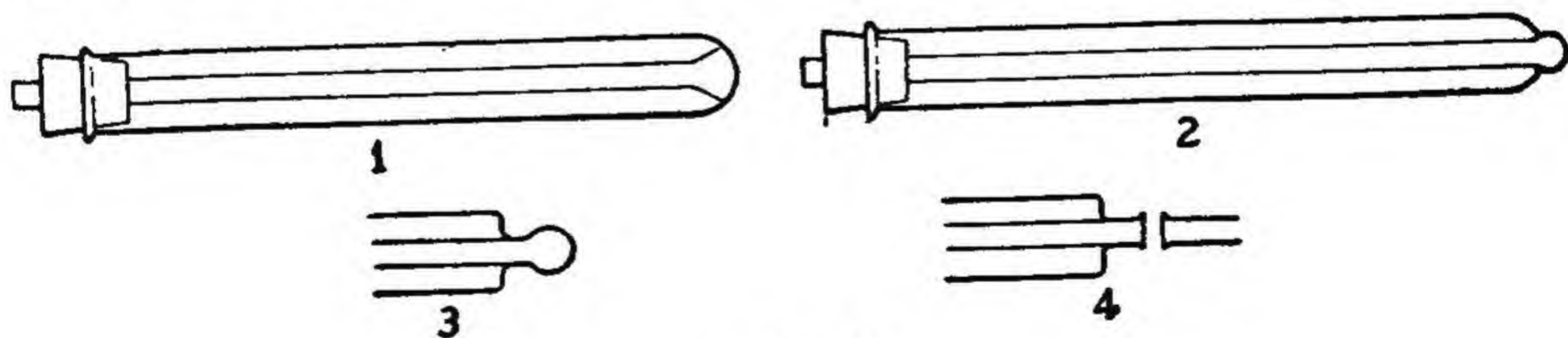


FIG. 4

Select a tube of about half the diameter of the large one and flange one end of it. Provide it with a cork that will fit the large tube, and file a groove along the outside of the cork to permit air to escape and place the small tube inside the large one with the



flanged end against the inside of the rounded end of the large tube (Fig. 4, (1)).

The closed end is now heated until the inner tube is sealed to the outer tube, and the weld made smooth and round by blowing in the center tube and through the grooved cork respectively.

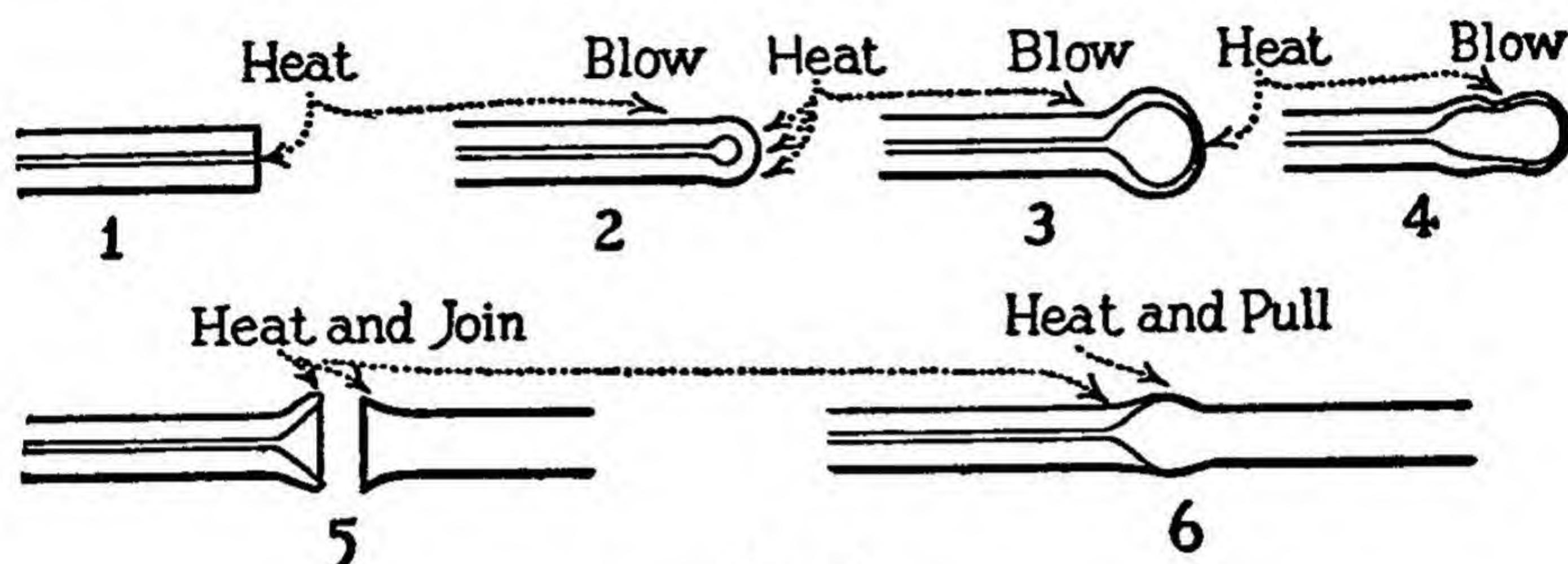


FIG. 5

A bubble is now formed at the closed end of the center tube, and a tube of the same diameter as the center tube sealed at the hole formed when the bubble bursts (Fig. 4). It will be noted that if the fragments of thin glass left when the bubble bursts are heated while the tube is rotated, they will draw back (surface tension) to the tube and form a thick walled ring to which a seal can easily be made.

Smooth up the seal, then heat carefully and anneal.

**Capillary Seals.** Obtain a piece of capillary tubing of 0.4–0.7 mm. bore. Let a drop of molten glass form at one end and blow in the other end to form a thick walled bulb. Heat the tip of the bulb and blow out a bubble large enough to leave a  $1/8''$  hole. Seal a piece of ordinary  $1/4''$  tubing to this hole (operations indicated in Fig. 5).

#### REFERENCES:

Waran, *Elements of Glass-Blowing*, Van Nostrand.

Frery, *Laboratory Manual of Glass-Blowing*, McGraw-Hill.

Woollatt, *Laboratory Arts*, Longmans.



## EXPERIMENT 1

### MOLECULAR WEIGHT OF VAPORS BY DUMAS METHOD

This experiment involves weighing a large bulb open to the air, filling it with the vapor of some pure substance at a known temperature and atmospheric pressure, sealing and weighing it, and finally weighing it filled with water. From the data so obtained, the volume of the bulb and the weight of the vapor and hence the volume occupied by a known weight of the substance at a known temperature and pressure can be ascertained.

**Directions.** Carefully clean a Dumas bulb, Fig. 6, and then dry it by warming (water-bath) and applying suction. For the

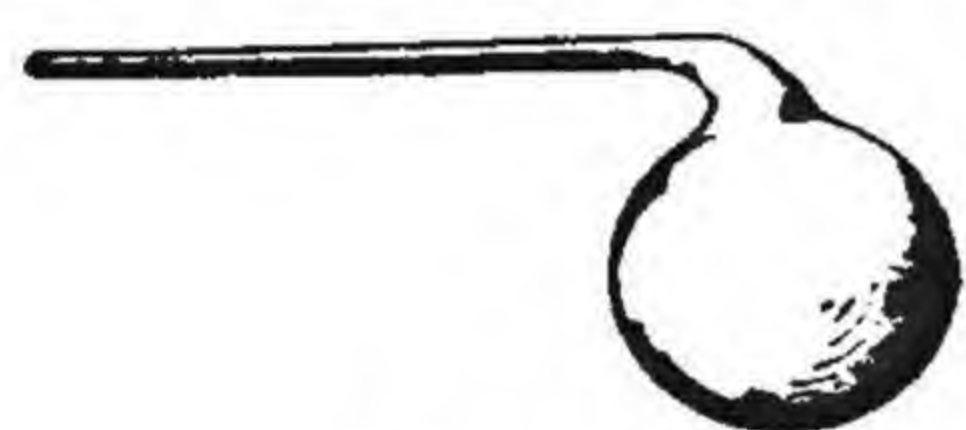


FIG. 6

latter purpose introduce (before drawing out the stem of the bulb to a capillary) a piece of small glass tubing. *Do not use alcohol and ether.* Draw out the stem of the bulb to a capillary, and when cold weigh it accurately. A second bulb may or may not

be used as a counterpoise, as desired. Introduce about 20 cc. of benzene into the bulb in the following manner. Fill an 800 cc. of beaker half full of tap water and heat to the boiling point. Immerse the bulb in the boiling water for half a minute, remove from the bath and at once put the tip under benzene. (The first few drops of benzene sucked into the bulb are vaporized and fill it with benzene vapor.) With the tip still under benzene, quickly cool the bulb with a wet towel. As much as 20 cc. of benzene can be easily drawn into the bulb in this manner. Remove the tip as soon as this amount has entered. Insert the bulb in a holder, provided for the purpose or made from a piece of heavy galvanized iron wire, and support the whole in a water-bath which has previously been heated nearly to  $100^{\circ}$  (about  $90^{\circ}$ ) so that only two or three centimeters of the tip are above the surface of the water. Raise the temperature until the bath begins to boil and keep it boiling gently. It is important that the temperature of the water-bath be kept constant especially at the time when the last traces of



excess liquid are being boiled out. After the bulb is once immersed in the bath it should not be removed for any purpose until the tip has been sealed. When the vapor has ceased to come out of the bulb, which can be easily ascertained by flashing the opening with a flame (do not use same burner for flashing and sealing the tip, as is used under the water-bath) remove by careful flashing any of the liquid which may have condensed in the exposed stem of the bulb and quickly seal the tip. A small Bunsen burner gives a suitable flame for the flashing test and for sealing the capillary. Read at the same moment the temperature of the bath and soon afterwards, the height and temperature of the barometer. Remove and dry the bulb, and when cold, weigh it accurately. Note at this time the temperature of the balance case. Fill the bulb with water by carefully filing and breaking off the tip (save) under cold distilled water from which air has been removed by boiling. If an air bubble remains, it does no harm and necessitates no correction, as long as the volume of water entering the bulb is taken as the volume of the vapor. Weigh the bulb filled with water on a large balance.

The experiment will involve obtaining acceptable duplicate results for the vapor density and molecular weight of some liquid such as benzene. The student may also obtain an unknown from the instructor.

**Calculations.** Calculate the density (grams per liter) of the vapor at the boiling temperature and the barometric pressure, and the corresponding molecular weight of the vapor under these conditions. To calculate the molecular weight of the substance under investigation use the perfect gas law. The barometric pressure must be corrected to 0° and reduced to atmospheres (see Exercise II).

$$pV = \frac{w}{M}RT$$

$M$  = molecular weight;  $w$  = weight of vapor;  $V$  = volume of water in the bulb (taking density of water = 1.00).

Since the important thing to determine in this experiment is the weight of the benzene vapor, which is the difference between the weight of the bulb full of vapor and the *empty* bulb, the weight of the air in the bulb must be taken into account. This weight can be calculated from the inside volume of the bulb and the



density of air at the barometric pressure and the observed temperature of the balance case. This amounts to making the correction for the buoyancy of air (see Exp. 9). This, of course, must be done, whether or not a counterpoise bulb is used in the weighing.

REFERENCES:

- Taylor, Chap. III.
- Rodebush, Chap. II.
- Getman and Daniels, Chap. II.
- Millard, Chap. II.
- Findlay, Chap. II.



## EXPERIMENT 2

### VAPOR DENSITY; VICTOR MEYER METHOD; LIMITING DENSITY METHOD

In Experiment 1, by the Dumas method, the vapor density or the molecular weight was determined by getting the *weight* of a known volume of vapor at a known temperature and pressure. In the Victor Meyer method the procedure is reversed. The *volume* of a known weight of vapor is measured. The present experiment is divided into two parts. In Part A a determination of molecular weight is made which, although only approximate in its results, is good enough for most purposes. Many students will be content to do this part alone. The largest error is introduced, generally, because vapors do not obey the perfect gas laws, and in Part B, the so-called method of "limiting density" will be described, as a means of obtaining the true molecular weight in spite of the failure of the equation  $pV = \frac{w}{M}RT$  (in the case of vapors or easily condensable gases).

#### (A) EXPERIMENTAL

Figure 7 shows the arrangement of the apparatus. A weighed amount of the working substance is introduced into the apparatus in a small bulb *b* which is supported on an iron trigger rod *G*, which can be pulled to the left with a magnet at the proper moment to allow the bulb to drop to the bottom of the inner tube *T*. Here the small bulb is broken and its contents volatilized. This vapor forces its own volume of air out of tube *T*, through the side arm *A* into the burette *B* (100 cc. capacity) filled with mercury. The volume of the displaced air is then measured with the aid of the leveling tube *L* and the leveling bulb *L.B.* The temperature is read from a thermometer which hangs alongside the burette. The pressure of the air in the burette, which is the pressure of the atmosphere if the mercury levels are the same, is determined with



a barometer. The inner tube T is heated in a vapor bath. In general the temperature of this bath should be  $20^{\circ}$ – $30^{\circ}$  higher than the boiling point of the substance to be volatilized. In the present experiment *water* is placed in the bottom of the outer

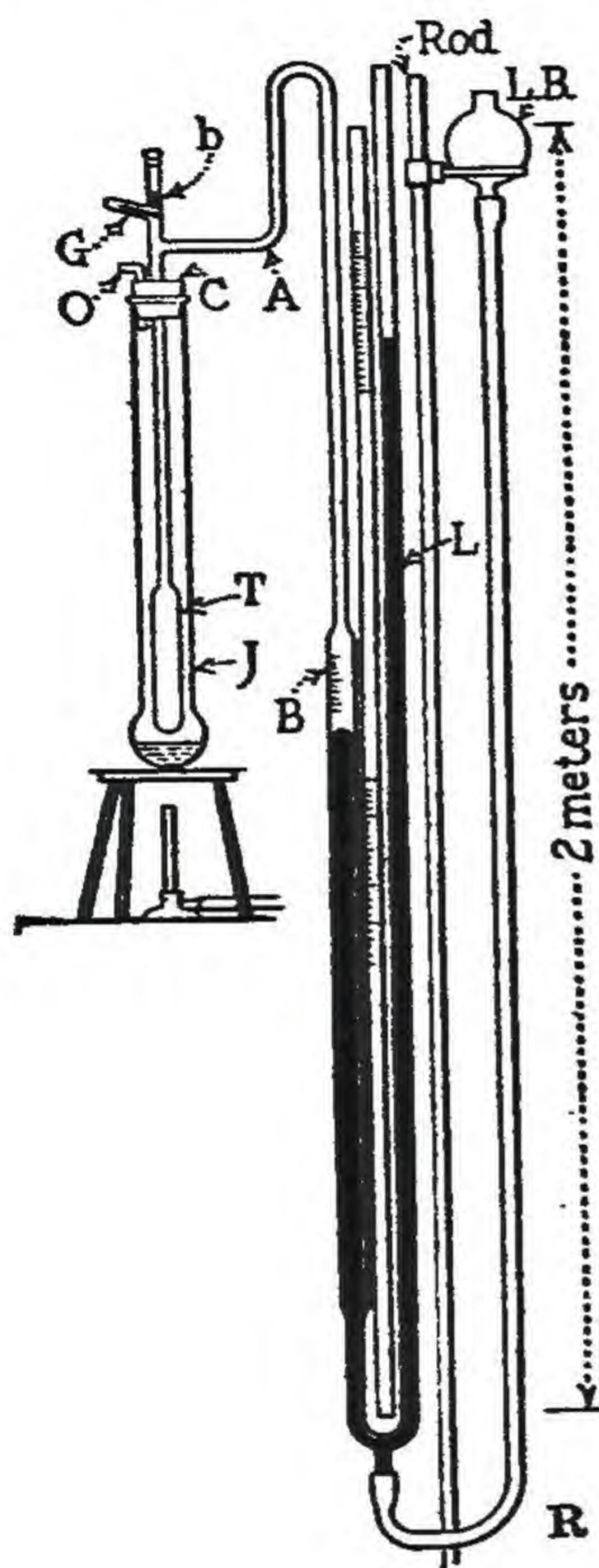
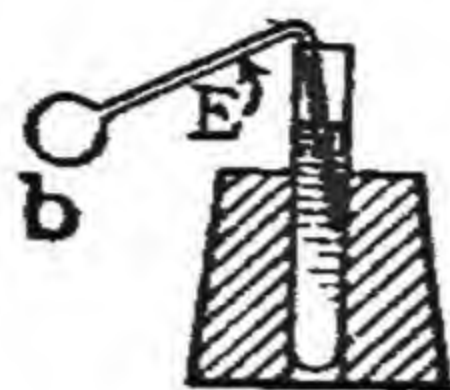


FIG. 7



jacket J, and is boiled over a gas flame. It is important to have the water vapor condensing well towards the top of the jacket, so that the entire enclosed length of tube T will be heated uniformly. The water vapor escapes through the exit tube O in the cork or rubber stopper C. It is desirable that the jacket be made of pyrex, as the life of soft glass jackets is not very long.

The student may or may not construct the inner tube T, using soft glass or pyrex, preferably the latter. If the student has had no experience in glass-blowing, he should consult one of the manuals on this subject provided on the laboratory book-shelf, or he should seek directions from the instructor, or he may get some help from Exercise IV.

The over-all length of tube T should be 65–75 cm., the bulb at the bottom should be 25–30 mm. in diameter and 25–30 cm. long, and the smaller tubing of about 8–10 mm. bore. The trigger rod G is to be made of a piece of small iron rod and slips back and forth easily in the glass side-arm. Heavy pressure rubber tubing must be used at R, and it should also be wrapped throughout the lower half of its length with friction tape to prevent bulging under the heavy weight of mercury.

If the student is going to do only Part A of this experiment, he



may, if he wishes, substitute a 50 cc. burette with a leveling bulb and use water instead of mercury. In that case, of course, the observed pressure must be corrected for the vapor pressure of water. The apparatus described here, employing mercury, is designed so that it may be used for both Part A and Part B.

When the apparatus has been assembled as described, make a dozen or more small bulbs *b* as follows. Draw out in a small, well-pointed blast flame a piece of soft glass tubing (3–4 mm. bore) into a chain of small capillaries separated by short accumulations of thicker glass. The capillaries should be a little less than 1 mm. outside diameter, and about 15–20 cm. long, that is there should be 15–20 cm. between the accumulations. Break the chain into smaller lengths by cutting the mid-point of the capillaries with a file. Each of these pieces may be made into two bulbs. Do this by heating the accumulation of glass in a needle-pointed flame, pulling apart, reheating the closed end, removing from the flame, and by blowing into the open end of the capillary to form a small bulb. The bulb should be 4–7 mm. in diameter, and of very thin glass, although not so thin that it will crush on handling. Then touch the middle of the capillary for an instant with the flame, so that it falls into a bend of about  $90^\circ$ . The bulb then has the form indicated in the upper right-hand corner of Fig. 7. With an hour's practice the student should be able to make several dozen bulbs of this sort.

A bulb is selected and weighed. It is filled by immersing the open end of the capillary in a liquid, and warming the bulb carefully with a small luminous flame. Some of the air is thus forced out and when the bulb is cooled, liquid runs over into it. By heating and cooling several times, the bulb and capillary can be filled. The capillary should then be sealed off at point *E* (the bulb may be cooled with ice if necessary) and the waste capillary is heated in the flame to drive out all adhering liquid. The filled bulb and the waste capillary are then both weighed, and the weight of the liquid obtained.

It is well to have a number of the small glass bulbs available, so that one of the proper size may be selected. If the bulb is too large, a volume of air larger than the capacity of the burette will be forced over, and if it is too small the accuracy of the determination will suffer.



When the water is boiling steadily, pull back the trigger G with a magnet and insert a long glass tube which reaches to the bottom of the hot inner tube T. Pass a stream of air, dried over calcium chloride, through T for several minutes to dry it out thoroughly. Withdraw the long tube, and place the filled and weighed bulb on the trigger, bring the mercury level near the top of the burette, and then force the rubber stopper above b securely into place. Again adjust the mercury levels, and let the system stand for a few minutes. Constancy of mercury level indicates an even temperature throughout the vapor bath. At this stage the apparatus should be tested for leaks by raising and lowering the leveling bulb to see if air can be drawn into, or forced out of, the system. Now pull the trigger and let the bulb drop. If it does not burst on striking the bottom, it will soon be broken by the expanding liquid, if the bulb has been properly made of thin glass, and if it has been almost completely filled with liquid. Determine the volume of air forced over into the burette, waiting a few minutes for the air to attain room temperature, before taking the final constant reading. If the air volume continues to shrink, it is an indication that some of the vapor has diffused into the cooler portions of the system and is condensing. In this case take the *maximum* volume as the final reading. Occasionally the air volume increases slowly. This indicates that some of the liquid is still trapped in the bulb or capillary and is being very slowly volatilized.

Make two duplicate determinations of the vapor density (in grams per liter) either of ethyl ether or of chloroform. Calculate the molecular weight. Obtain an unknown liquid from the instructor and determine its molecular weight. The results should check within 2 to 4 per cent of the theoretical values.

In the Victor Meyer method, what difference would be found in the final results if the jacket bath had been kept at a temperature of  $184^{\circ}$  (boiling aniline) instead of at  $100^{\circ}$ ?

### (B) LIMITING DENSITY METHOD

(1) Using either pure  $\text{CS}_2$  or pure  $\text{CH}_3\text{COO} \cdot \text{CH}_3$  as the working substance, determine the molecular weight as accurately as possible as in (A), but select a bulb b of proper size to hold enough



of the working substance to give about 50 cc. of air displacement in the mercury burette. Make the first determination at atmospheric pressure, as in (A). (2) Then clean and dry the apparatus and select a bulb b of about one-half the volume of the first one. Bring the mercury level, at atmospheric pressure, near the top of the burette, insert bulb and *close the apparatus* with the rubber stopper, above bulb b, securely. Now lower the mercury about half way down the burette, note the volume reading, *and* the pressure reading. The air pressure in the apparatus is now considerably below atmospheric, and the pressure can be obtained by subtracting the manometer reading from the barometric pressure. Then allow bulb to fall and break, and measure the volume displaced *at the same lowered pressure* as before the displacement. (3) Repeat with a bulb b, about twice as large as in (1), starting with the mercury near the bottom of the burette, closing the system, and *increasing* the initial pressure much above atmospheric by raising the leveling bulb L.B., and finally after breaking bulb b, getting the volume of displacement at the same high pressure.

The  $pV$  products of the air in the apparatus, which are the same before and after the displacement, cancel out; and thus it is possible to calculate the  $pV$  products of the vapor at the three different pressures. Calculate these all to a basis of 1 gram of the working substance, in any convenient units, say in mm.-liters, and plot them as ordinates against pressure as abscissas. Extrapolate to zero pressure, and substitute the resulting  $pV$  value in the equation  $pV = \frac{1}{M}RT$  to get the true molecular weight  $M$ . It is desirable to get more than three  $pV$  values, working over the range between the smallest and largest pressures attainable with the apparatus.

**REFERENCES:**

- Taylor, Chap. III.
- Rodebush, Chap. II.
- Getman and Daniels, Chap. II.
- Millard, Chap. II.
- Findlay, Chap. II.



### EXPERIMENT 3

#### DETERMINATION OF THE VAPOR DENSITY AND THE MOLECULAR WEIGHT OF ACETIC ACID VAPOR BY A DYNAMIC METHOD

**Principles Involved.** Dalton's Law of Partial Pressures and the relation  $pV = \frac{w}{M} RT$ .

**Method.** A measured volume of  $\text{CO}_2$ -free air (2 liters) is passed over "anhydron" ( $\text{MgClO}_4$  on asbestos) to remove the water vapor. The dried air is then saturated with acetic acid vapor by passing it slowly through a bubbler filled with acetic acid. The bubbler is maintained at a constant temperature in a hand-regulated thermostat, a few degrees below room temperature to prevent condensation in ground joint  $p$  and cock  $g$ . The air, saturated with acetic acid vapor, is then passed through a weighed U-tube containing "ascarite" ( $\text{NaOH}$  on asbestos). Here the acetic acid is absorbed, and its weight is determined by a second weighing of the absorption tube.

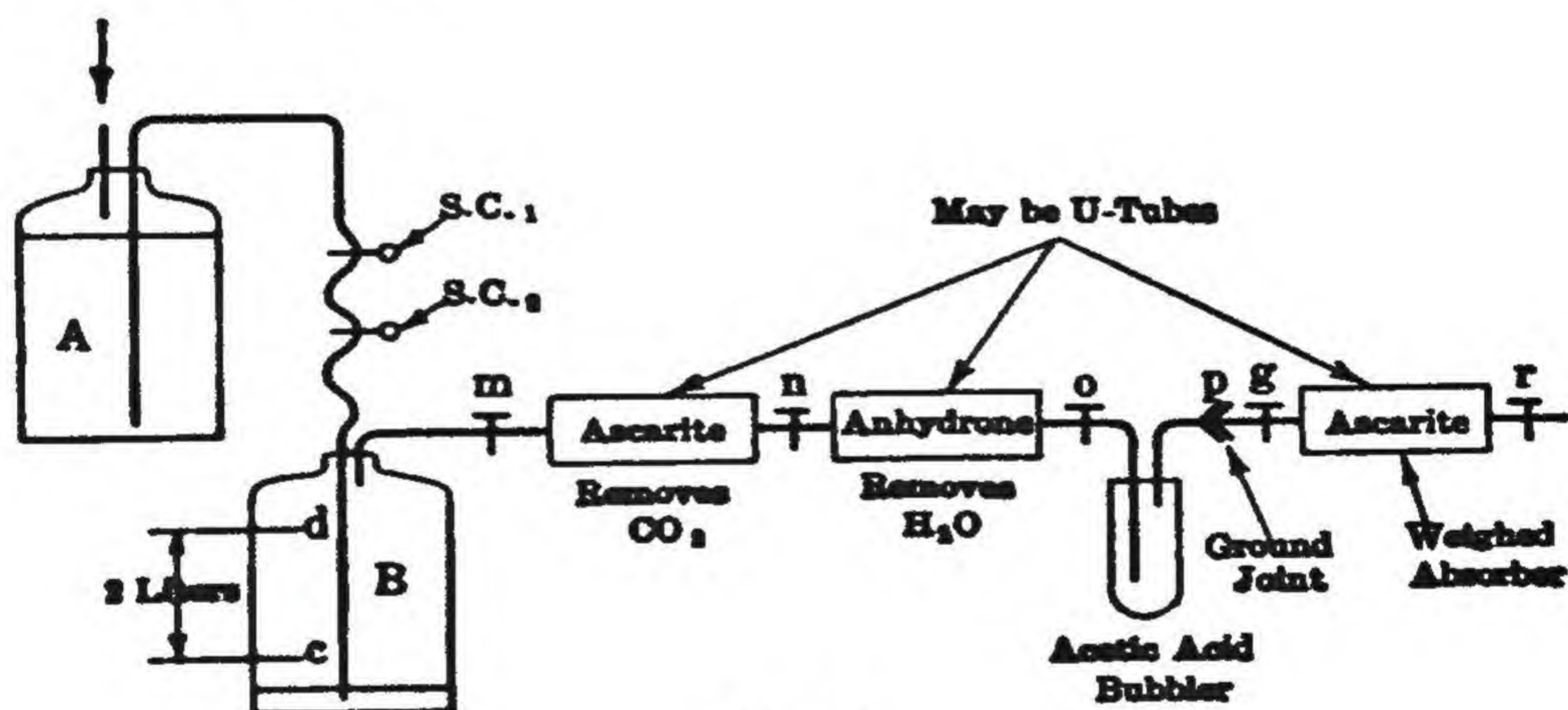


FIG. 8

**Procedure Filling B.** With the "train" removed, Fig. 8, the calibrated 2-liter bottle B is siphoned full of water by opening the two screw clamps, S.C.1 and S.C.2. The first ascarite tube alone is then connected at  $m$ , B is elevated above A, and one of the screw clamps is adjusted so that 15 or 20 minutes is required to



## DETERMINATION OF THE VAPOR DENSITY 45

fill B with  $\text{CO}_2$ -free air. When B is filled, the screw clamp is closed, and the bottles are returned to the positions shown in the figure.

**Testing for Leaks.** The rest of the train is then connected as shown above, and the entire line is tested for leaks as follows. Valve  $r$  is closed, all other valves and clamps are opened, and the constancy of the water level in A (or B) is observed. The student should be very critical in this test and should not proceed until the line is proved to be free of leaks.

**Adjusting Rate of Flow.** The train is now disconnected at  $n$  and the rate of flow of air is set at about 2 liters per hour by adjustment of screw clamp 1. The level in B is then permitted to rise to mark  $c$ . Without changing the adjustment of screw clamp 1, clamp 2 is closed tight when the level is exactly at  $c$ .

**Weighing the Absorber.** The ascarite absorber at the end of the train is disconnected, and the grease is removed from its ground joint  $p$  by wiping it several times with small swabs of xylene-soaked cotton on the end of a match stick. Finally, with its valves closed, the absorber is weighed to 0.1 milligram.

**The Experiment.** The joint of the absorption vessel is carefully re-greased, and the vessel is replaced in the line. (In the meantime a one-liter beaker of water has been brought to  $30^\circ \pm 0.50^\circ \text{C}$ . and the acetic acid bubbler has been immersed in it.) When the acetic acid has had time to assume the temperature of the thermostat, all valves in the line are opened, and screw clamp 2 is removed. The thermostat is maintained at  $30^\circ \pm 0.5^\circ$  throughout the run.

**Final Weighing.** When the level in B is close to  $d$ , A is lowered and supported so that the level in A is not more than 4 cm. above that in B at the moment when the level in B reaches the mark  $d$ . Valves  $g$  and  $r$  are closed at once, the absorber is disconnected, the grease is removed from the joint as before, and the final weighing is made.

**Calculations.**

$$(p_B - p_{\text{H}_2\text{O}}) \cdot V_1 = N_A R T_1. \quad (1)$$

$$(p_B - p_{\text{HAc}}) \cdot V_2 = N_A R T_2. \quad (2)$$

$$d = \frac{w}{V_2}. \quad (3)$$

$$p_{\text{HAc}} \cdot V_2 = \frac{w}{M} R T_2. \quad (4)$$



$p_B$  = barometric pressure.

$p_{H_2O}$  = vapor pressure of water at  $T_1$  (look up table of aqueous tensions).

$p_{HAc}$  = vapor pressure of acetic acid at  $T_2$  (see table at end of this chapter),

$T_1$  = room temperature = temp. of air in calibrated bottle B.

$T_2$  = temperature of the thermostat containing the HAc bubbler.

$V_1$  = volume of moist air expelled from bottle B = 2 liters.

$V_2$  = volume occupied by dry air + acetic acid vapor at  $T_2$ .

$N_A$  = number of mols of dry air passed.

$w$  = weight of HAc absorbed in the final absorption tube.

$d$  = density of HAc vapor at  $T_2$  (to be calculated).

$M$  = molecular weight of acetic acid vapor (to be calculated).

$N_A$  is calculated from (1),  $V_2$  from (2), the density  $d$  from (3) and the molecular weight  $M$  from (4). In the last calculation the vapor pressure of HAc at  $T_2$  must be known. This can be obtained from the following table.

TABLE V

$t^\circ \text{C.}$	$p_{HAc}$ in mm. of Hg	$t^\circ \text{C.}$	$p_{HAc}$ in mm. of Hg
25	15.6	31	21.7
26	16.5	32	22.8
27	17.5	33	24.1
28	18.5	34	25.4
29	19.5	35	26.7
30	20.6		

If the molecular weight,  $M$ , of the volatile substance is known in the vapor state, this method may be used, conversely, to determine the vapor pressure.

#### REFERENCES:

Taylor, Chap. III.

Rodebush, Chap. II.

Getman and Daniels, Chap. II.

Millard, Chap. II.

Findlay, Chap. II.



## EXPERIMENT 4

### RATIO OF SPECIFIC HEATS (OR OF MOLAR HEATS)

Some very interesting and instructive results come out of a consideration of the specific heats of gases. The specific heat of a substance is the quantity of heat required to raise 1 gram of that substance  $1^{\circ}\text{C}$ . Since the specific heat varies (increases) with increasing temperature, it is of course necessary to specify the temperature. For our present purpose we shall find it more convenient to deal with molar heats than with specific heats. The molar heat is the heat required to raise the temperature of 1 mol  $1^{\circ}\text{C}$ ,  $C = M \cdot c$ , where  $C$  symbolizes molar heat,  $c$  specific heat, and  $M$  molecular weight.

We recognize two different kinds of molar heats (and also specific heats): (1) The molar heat at constant volume,  $C_v$ , where the substance whose temperature is being raised  $1^{\circ}\text{C}$ ., is not allowed to change its volume; and (2), the molar heat at constant pressure,  $C_p$ , where the volume of the substance being heated is allowed to increase, but the pressure to which the system is being subjected at the end of the heating is the same as at the beginning. In the case of gases,  $C_p$  is rather easily measured at ordinary temperatures (Rodebush, p. 29), but it is a difficult matter to measure  $C_v$ . The molar heat at constant volume,  $C_v$ , is the same for certain gases, and for other gases it is different. But, whatever the actual value of  $C_v$  may be, it can be shown by experimental measurement that  $C_p$  is always just  $R$  calories larger than  $C_v$  for all gases (except under conditions where there are serious departures from the gas laws).  $C_p = C_v + R$  calories. This is what we would expect from theory, because when a gas is heated at constant pressure, not only must enough heat be put into the gas to raise its temperature  $1^{\circ}\text{C}$ ., but also to do the work of expansion against the atmosphere. Quantitatively, this extra heat is given by the equation

$$p(v_2 - v_1) = R(T_2 - T_1) \quad (1)$$

where  $v_1$  and  $T_1$  are the initial, and  $v_2$  and  $T_2$  the final volume and temperature. If  $T_2 - T_1 = 1^{\circ}$ , then the mechanical work of



expansion,  $p(v_2 - v_1) = R$  calories. Hence  $C_p$  will be greater than  $C_v$  by  $R$  calories, approximately 2 calories.

The magnitude of  $C_v$  depends on the complexity of the gas molecule, and  $C_v$  is the quantity in which we are most vitally interested in the present discussion. But it is very useful to deal in terms of the ratio of the two molar heats  $C_p/C_v$  (which is symbolized by the Greek letter gamma,  $\gamma = C_p/C_v$ ), because of the relative ease with which  $\gamma$  is determined experimentally. From what has just been previously said it follows that

$$\gamma = \frac{C_v + 2}{C_v}. \quad (2)$$

Obviously if  $C_v$  is known,  $\gamma$  can be calculated; and if  $\gamma$  is known,  $C_v$  can be calculated.

Let us now attempt to predict on purely theoretical grounds, the values for  $C_v$  for some gas molecules of different types.  $C_v$  is the heat poured into a mol of gas at constant volume to raise the temperature  $1^\circ$ . This heat is used up by the molecules of the gas to increase their kinetic energy. In general the kinds of motion which thereby become more violently excited are translation, spin, and oscillation.

**Monatomic Molecules.** The only type of motion which monatomic molecules, like helium, can execute is translatory motion. Single atoms are not easily started spinning; i.e. they do not easily acquire "English" as a billiard ball does. Other atoms and molecules which bump into them simply skid off; the spin does not take hold, because most of the mass is located in the nucleus at the center of the atom. Neither does oscillation occur with single atoms. At least two atoms, each held within the attractive force field of the other by elastic forces along the line of juncture, are needed for oscillation. Since the kinetic energy of translatory motion for a mol of gas is given by the equation  $K.E. = \frac{3}{2} RT$  (Rodebush, p. 30), the molar heat at constant volume,  $C_v$ , for a monatomic gas will be  $\frac{3}{2} R$  calories, or approximately 3 calories (since  $T_2 - T_1 = 1^\circ$ ). Therefore  $\gamma = \frac{3 + 2}{3} = 1.66$  for a monatomic gas.

Further, since the increase in translatory motion (in 3 dimensional space) which results from the rise of  $1^\circ$  in temperature, can



be described in terms of velocity components along  $x$ ,  $y$  and  $z$  axes, we find it helpful in our analysis of the situation to say that there are three types of motion, namely in the  $x$ ,  $y$  and  $z$  directions, and to call every one of these types of motion a "degree of freedom." Thus the molecules of helium possess three degrees of freedom. Moreover since we must think of the  $x$ ,  $y$  and  $z$  motions as being all equally probable, that is since we must think of the gas as being isotropic with respect to molecular velocities, the Principle of the Equipartition of Energy tells us that the 3 calories of heat must be partitioned out equally among the three degrees of freedom, 1 cal. for  $x$ -motion, 1 for  $y$ -motion and 1 for  $z$ -motion.

**Diatomic Molecules.** Now in the case of diatomic molecules, such as oxygen ( $O_2$ ), the molecules cannot only absorb heat, when the temperature is raised  $1^\circ$ , by increasing their  $x$ ,  $y$  and  $z$  translatory motions, but also the molecules can spin about two axes, when sufficiently stimulated. In Fig. 9(b) a crude dia-

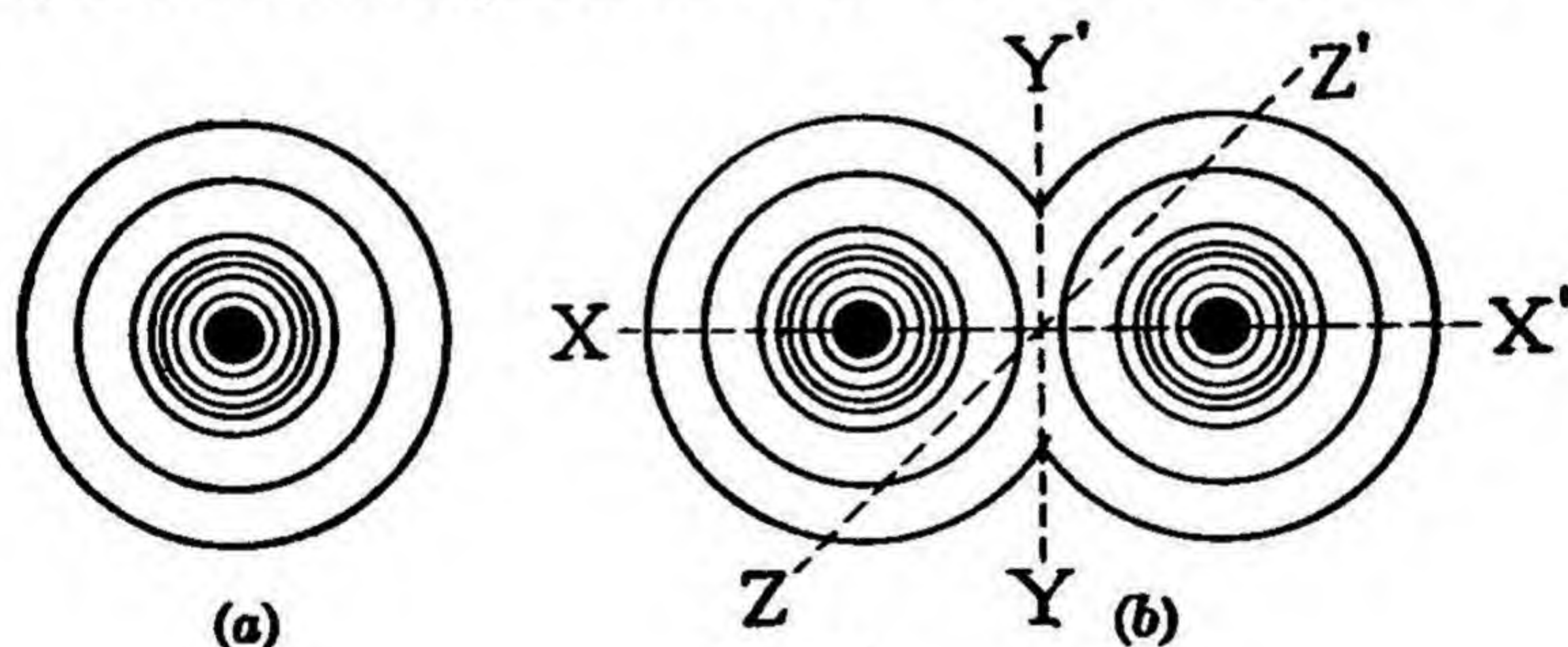


FIG. 9

grammatic representation is given of such an oxygen molecule. Most of the mass of the molecule is concentrated in the two nuclei; the extra-nuclear electrons, which make up only a very small fraction of the total mass anyhow, are scattered through a much larger volume, with a density of distribution which falls off exponentially with increasing distance from the nuclei (Rodebush, p. 357), as indicated roughly by the density contour lines. The two heavy nuclei can spin like a fly-wheel, around the center of gravity of the molecule; at least spin can occur about the  $Z - Z'$  and  $Y - Y'$  axes. The energy of this rotational spin,  $E_r$ , is given by the following equation (Rodebush, p. 31)

$$E_r = \frac{n(n+1)h^2}{8\pi^2 I} \quad (3)$$



where  $n$  may have the values 0, 1, 2, 3, 4, . . . ,  $h$  is the Planck constant and  $I$  is the molecule's moment of inertia. The moment of inertia is the sum of all the products of the masses of the nuclei into their radial distances from the center of gravity, namely  $\sum mr^2$ .

The rotational motion just referred to is quantized; that is to say, a molecule will not gradually increase its velocity of spin from low to high, like a fly-wheel, but it increases by steps. It will not start to spin at all unless it receives a certain minimum quantity of energy, a quantum of energy, the size of which is characteristic of the molecule, and is given by Equation 3 above, when  $n = 1$ . The spin motion can then be further excited by the acquirement of rotational energy which is a multiple of the original quantum, as given by Equation 3. This equation shows that the magnitude of the quantum of energy is inversely proportional to the moment of inertia  $I$ . When  $I$  is relatively large,  $E_r$  is relatively small, and there is a good probability that even at ordinary temperatures the average molecule will be bumped hard enough by the impacts of other molecules to start it spinning, at least about  $Z - Z'$  and  $Y - Y'$  axes, but not about the  $X - X'$  axis. About  $X - X'$  axis, Fig. 9(b), the moment of inertia is exceedingly small, since most of the mass is situated on the axis, and the only mass in the expression  $\sum mr^2$  is the mass of the electrons. No doubt at enormously high temperatures spin about the  $X - X'$  axis could be excited. But at ordinary temperatures little if any of this type of rotation occurs, because of the very large quantum required; and for the same reason monatomic molecules, Fig. 9(a), do not pick up spin, as we have already stated. (In these considerations we are not discussing nuclear spin.)

In the case of diatomic molecules the two rotational degrees of freedom, about  $Z - Z'$  and  $Y - Y'$  axes, each absorb 1 cal., according to the Equipartition Principle, for a rise of  $1^\circ$  in temperature. The point is that there is a give and take of energy between all the different modes of motion among the molecules of a gas, and the spin motions get just as large a share of the heat energy poured into a gas when its temperature is raised as do the  $x$ ,  $y$  and  $z$  translatory degrees of freedom. Consequently, for a



diatomic gas we would expect  $C_v$  to be  $3 + 2$  calories; and  $\gamma = \frac{3 + 2 + 2}{3 + 2} = 1.40$ .

It is to be noted, however, that all of the molecules in a swarm of diatomic gas molecules need not necessarily be spinning. The energy-rich molecules may be spinning; the molecules poorer in energy may be undergoing translatory motion alone. Whether all of the molecules are excited to spin, or what fraction of the total is excited, will depend not only on the moment of inertia of the molecule, but also on the temperature.

But there is still another type of motion which must be taken into consideration in the case of diatomic molecules, namely vibration or oscillation. In Fig. 9(b) the two oxygen atoms can approach one another, and recede from one another, oscillating back and forth. This type of motion is also quantized, like spin motion; translatory motion is not. The magnitude of the quantum required to excite the oscillation is greater the tighter and stronger the chemical bond uniting the atoms. For many tight-bond molecules, such as  $H_2$ ,  $O_2$ ,  $CO$ ,  $N_2$ , the oscillation is frozen, that is, it is not excited, at ordinary temperatures. But at sufficiently high temperatures the oscillation may become violent and of large enough amplitude so that the atoms fly apart and the molecule dissociates. In oscillation of this sort both kinetic energy and potential energy are involved. When the atoms are closest together the energy is all potential (repulsion), at the equilibrium distance it is kinetic, and at the distance of greatest separation it is again potential (attraction). In this respect each atom behaves somewhat like the bob of a swinging pendulum. To each such oscillation degree of freedom (per mol of gas for  $1^\circ$  rise in temperature) 2 calories of heat must be assigned, for while the kinetic energy is being continuously changed into potential energy, and vice versa, there are always two moving parts in the oscillation.

Thus in a loose-bond diatomic molecule  $C_v$  would be (3 translation + 2 spin + 2 oscillation) calories, and  $\gamma = \frac{7 + 2}{7} = 1.286$ .

For diatomic molecules therefore  $\gamma$  may have the value 1.40 for tight bonds, or 1.286 for loose bonds, or any value between these two figures, depending on the strength of the bond, and on the



extent to which certain fractions of the total numbers of molecules may have their oscillation motions excited at any particular temperature. The relative numbers of molecules in the different excited energy states, both spin and oscillation, can be calculated by means of the Boltzmann factor treatment,  $e^{-E/RT}$ . (See Exercise III.)

**Triatomic Molecules.** In the case of triatomic molecules, like  $\text{SO}_2$  or  $\text{O}_3$ , which do not have their atoms all arranged on a single axis of rotation, there will be 3 degrees of spin motion, and  $\gamma$  will be  $\frac{3 + 3 + 2}{3 + 3} = 1.33$ . To the extent to which oscillation degrees of freedom are also excited,  $\gamma$  will be smaller than this.

**Polyatomic Molecules.** All polyatomic molecules will possess 3 translatory degrees of freedom and generally 3 rotational degrees of freedom. The more complex the molecule is, the larger will be the number of possible oscillation degrees of freedom, and the smaller will be the value of  $\gamma$ ; although it does not necessarily follow that all possible types of oscillation will be excited.

#### Exercises for the Student.

(1) At this point the student should make a list of the ratios of molar heats (or specific heats) for a score or more of the common gases (given in any good table of physical constants, such as the Chemical Rubber Publishing Company's Handbook of Chemistry and Physics, 18th Edition, pp. 1025-27) and determine for himself how well the predictions made above are borne out by the actual values of  $\gamma$ , and try his own hand at assigning the different kinds of degrees of freedom to the various molecules.

(2) Why does  $\gamma$  vary with temperature?

(3) Explain why the  $\text{H}_2$  molecule behaves like a monatomic molecule at very low temperatures, and why its  $\gamma$  assumes a value of about 1.32 at  $2000^\circ \text{C}$ . Calculate  $C_v$  for  $\text{H}_2$  from the various values of  $\gamma$  given in the Handbook table, and plot  $C_v$  as a function of temperature.

(4) Calculate the moments of inertia, in c.g.s. units, for the following molecules from the internuclear distances given:

$\text{H} - \text{H}$ ,  $0.76 \times 10^{-8} \text{ cm.}$ ;  $\text{I} - \text{I}$ ,  $2.80 \times 10^{-8} \text{ cm.}$ ;

$\text{O} - \text{O}$ ,  $1.2 \times 10^{-8} \text{ cm.}$ ;  $\text{H} - \text{Cl}$ ,  $1.28 \times 10^{-8} \text{ cm.}$ ;

in  $\text{CH}_4$ :  $\text{C} - \text{H}$ ,  $1.08 \times 10^{-8} \text{ cm.}$



A strictly quantitative treatment of this whole matter of heat capacity is naturally beyond the scope of this manual. Enough has been said in the foregoing brief theoretical treatment to show the significance of  $\gamma$ , the ratio of specific heats, and to indicate how a determination of its actual experimental value for a given gas may tell us something about the types of motion which the molecules of the gas are executing. The student is urged in this general connection to consult the references at the end of this chapter, particularly Eucken, Jette and LaMer.

### EXPERIMENTAL

The value of  $\gamma$  may be conveniently determined by two experimental methods, (A) the Kundt method, and (B) the Clement and Desormes' method.

#### (A) KUNDT'S METHOD

The velocity with which sound travels through a gas can be expressed by the equation

$$u = \sqrt{\gamma \frac{p}{d}} \quad (2)$$

where  $u$  = the velocity of sound,  $p$  = the pressure and  $d$  = the density of the gas, and  $\gamma$  = the ratio of the specific heats. This equation has been established both experimentally and theoretically (a derivation is given in Edser, *Heat for Advanced Students*, pp. 325-9). Show that the quantities on the right-hand side of the equation have the dimensions of velocity. Since the pressure and density of a gas are easily determined, the value of  $\gamma$  can be calculated if the velocity of sound in the gas can be measured.

### EXPERIMENTAL

The apparatus consists of a glass tube, Fig. 10, about 1.5 meters long and about 3.5 cm. in diameter, closed at one end with a metal or cork cap B, through the center of which passes a long brass rod F carrying a cork or wooden piston D, which fits loosely inside the glass tube. The rod F is fastened securely *near its middle* (not shown in figure) with a set screw, to the cap B. At the other end of the tube is a piston E attached to a rod which can be moved in



and out through cap A. A little dry cork dust or lycopodium powder is sprinkled uniformly in the tube throughout most of its length. A current of air dried by passage through anhydrous calcium chloride is forced slowly through the tube, by using the inlet C and outlet G, and when the tube has been thoroughly washed out with the dry air, the screw clamps C and G are closed. The rod F is stroked or rubbed longitudinally with a piece of cloth



FIG. 10

(such as a towel) dusted with powdered rosin, until the rod vibrates strongly. The vibration is transmitted by the piston D to the air, and the sound waves which travel down the tube are reflected at E and set up an interference train (stationary vibration) when the position of E is adjusted so that the distance from D to E is an exact number of half wave-lengths. The powder in the tube becomes piled into little heaps during the vibration, with the heaps at the vibration nodes. The distance between heaps is one-half a wave-length. Obtain the average wave-length in cm. Shake the powder again into a uniform layer and redetermine the average wave-length. Repeat the determination with the tube filled with (1) dry oxygen and (2) dry carbon dioxide, and with any other pure gases which are available.

It is possible to find the vibration frequency of the rod F with a set of standard tuning forks, and then substitute the value for the velocity of sound (the product of wave-length and frequency) directly in Equation 2, together with the pressure and density and solve for  $\gamma$ . The student may, however, avoid the determination of the frequency by taking the velocity of sound in air as known, and then calculating  $\gamma$  for oxygen and carbon dioxide. In the case of oxygen,

$$\frac{\text{velocity in oxygen}}{\text{velocity in air}} = \frac{n\lambda_{\text{oxygen}}}{n\lambda_{\text{air}}} = \frac{\lambda_{\text{oxygen}}}{\lambda_{\text{air}}} \quad (3)$$

where  $n$  = frequency and  $\lambda$  = wave-length. Since the rod F vibrates at a common frequency for all of the gases used,  $n$  cancels out in the numerator and denominator. The velocity of sound



in air may be taken as

$$u = 332(1 + 0.00182 t) \text{ meters per second,} \quad (4)$$

where  $t$  is expressed in degrees Centigrade. Calculate the velocity of sound in air at the temperature of the Kundt experiment, and substitute in Equation 3 to get the velocity in oxygen. When this velocity is substituted in Equation 2, if it is expressed in cm./sec., in what units must the pressure and density be expressed when solving for  $\gamma$ ?

From the values of  $\gamma$  obtained for oxygen and carbon dioxide, indicate the number of degrees of freedom, translational, rotational and vibrational, possessed by a molecule of these two gases at room temperature. Do the same for any other gases available.

#### (B) METHOD OF CLEMENT AND DESORMES

When a gas is allowed to expand (or is compressed) isothermally the relationship between the initial and final volumes and pressures is given by Boyle's law, namely,

$$\frac{p_i}{p_f} = \frac{v_f}{v_i} \quad (1)$$

When, however, the expansion or compression is adiabatic the relationship is

$$\frac{p_i}{p_f} = \left( \frac{v_f}{v_i} \right)^\gamma \quad (2)$$

where  $\gamma$ , the ratio of the specific heats, occurs as an exponent in the volume term. (For a derivation of this equation, see Edser, *Heat for Advanced Students*, 313-21. Also see Lewis and Randall, *Thermodynamics*, pp. 64-5; and Taylor, *Elementary Physical Chemistry*, pp. 102-3; and Eucken, Jette and LaMer, pp. 82-3.) If a gas is expanded adiabatically and  $p_i$ ,  $p_f$ ,  $v_i$ ,  $v_f$  can all be measured, the equation can be solved for  $\gamma$ . This is the principle involved in the Clement and Desormes' method.

#### EXPERIMENTAL

A large glass bottle or carboy of 40-50 liters capacity is provided with a rubber stopper through which are inserted glass tubes as shown in Fig. 11. Air is led into the bottle B through the



drying tower A, with the stop-cock C open and F closed, and the rubber stopper D loosened so that the air can escape. After washing out the bottle B for 10–15 minutes with a rapid flow of dry air, open stop-cock F, tighten stopper D in the neck and gradually close C, so that a pressure somewhat above atmospheric is built up in the large bottle. The excess pressure should be 20–25 cm. on the manometer scale. A safety valve consisting of a glass tube running from the carboy under a small head of mercury M prevents an accidental blowing out of the manometer liquid by too great a pressure.

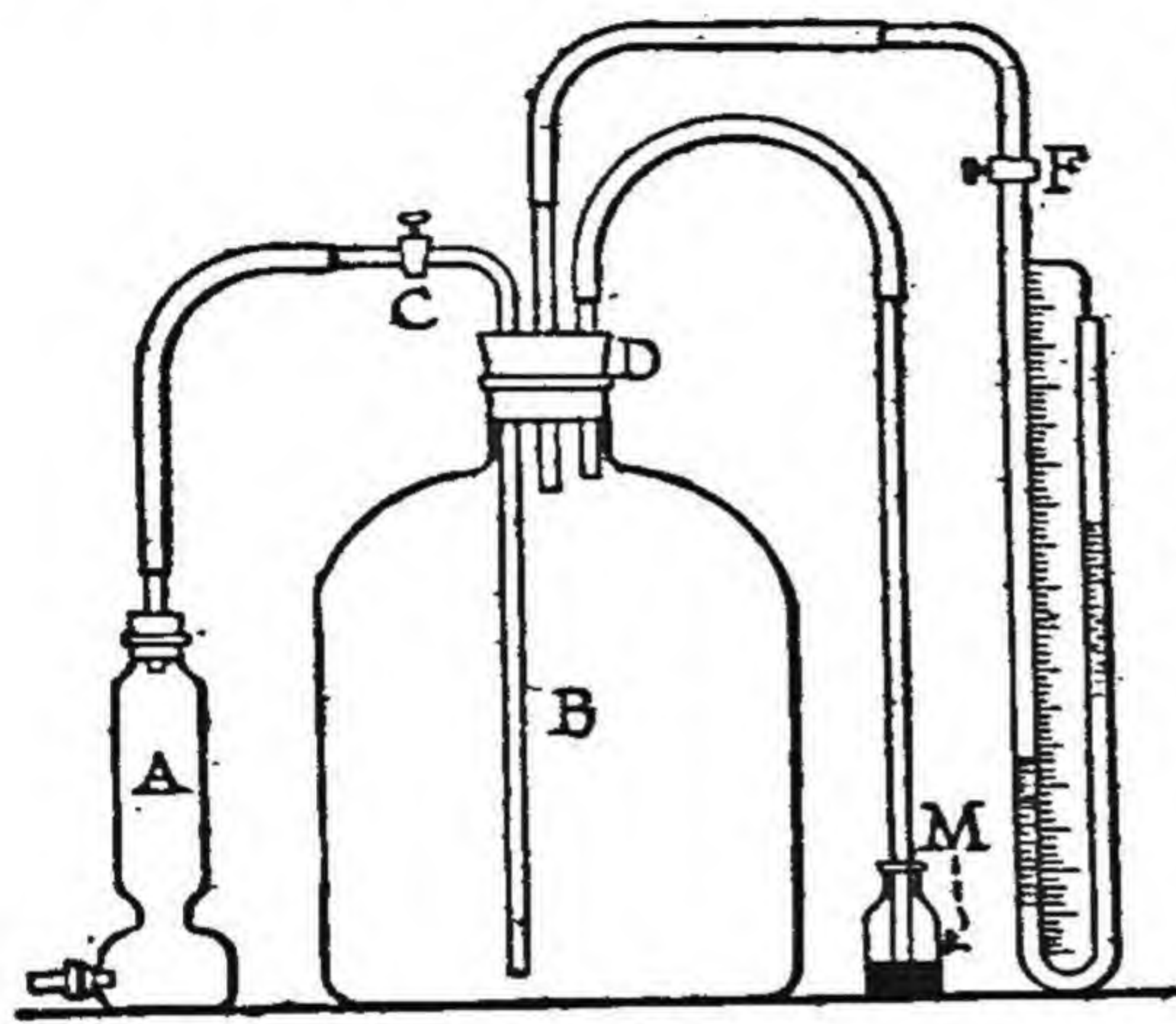


FIG. 11

For the sake of greater accuracy, it is better to use a liquid of small density rather than mercury in the manometer. Benzyl benzoate (density at room temperature = 1.12), because of its low vapor pressure, makes an excellent manometer liquid.  $\alpha$ -brom-naphthalene (density = 1.48 at 25° C.) and methyl salicylate (density = 1.18 at room temperature) also make good

manometer liquids. The readings on this manometer must then be converted to the values which would be obtained if mercury were used at 0° (see Exercise II). Density of mercury = 13.6. After the slight excess pressure has been produced, let the apparatus stand until the air in the bottle has attained room temperature, indicated by the constancy of the manometer readings. Note the final reading carefully. The pressure  $p_i$  of the confined air is equal to the barometric pressure (since one end of the manometer is open to the air) plus the manometer reading, in mm. of mercury.

Now open the bottle by lifting stopper D for an instant and immediately close it again. (The exact manner in which the stopper is replaced and the precise instant of replacement have a good deal to do with the final result, but we cannot discuss here the studies that have been made of this effect.) At this moment the liquid columns in the manometer arms stand at the same level, showing that the pressure inside the bottle is atmospheric. Some



of the air has escaped, and the expansion has been so rapid that no appreciable quantity of heat has flowed into the air from the surroundings, and hence the expansion is adiabatic. The end pressure of this expansion, namely atmospheric, is the  $p_f$  of Equation 2. The air in the bottle has been cooled, and it should be allowed to stand until it again attains room temperature. As it warms up, its pressure rises as indicated by the manometer. Let  $p_b$  represent this bottle pressure of the confined air (atmospheric pressure plus final manometer reading). All the data needed for the calculation of  $\gamma$  are now available. Repeat the experiment as a check.

The capacity of bottle B must be made large to make sure that the expansion is really adiabatic. Gases other than air may be employed in this experiment if desired, but the quantities required to displace all of the air, and to fill the bottle with pure gas, are rather large.

Calculation of  $\gamma$  from the data:

In the equation

$$\frac{p_i}{p_f} = \left( \frac{v_f}{v_i} \right)^\gamma \quad (2)$$

$p_i$  and  $p_f$  have been measured by the student, and  $v_i$ , the volume of the bottle, *could* be measured. The only thing needed to permit the calculation of  $\gamma$  is  $v_f$ , the volume of the gas after adiabatic expansion. This volume would be very difficult, if not impossible, to measure, since part of the gas has escaped and occupies a small volume outside the bottle. But by using a little strategy we can get the value of  $v_f$ , or at least the ratio  $v_f/v_i$ . After the stopper is replaced and the gas in the bottle is allowed to return to room temperature, we may imagine the small volume of gas outside as being also confined within rigid walls, and as being allowed to come back to room temperature. In this way the entire volume of gas  $v_f$  would at room temperature have a pressure  $p_b$ , the final measured pressure of the gas in the bottle, and since the volume of gas  $v_f$  would now be at the same temperature as the initial volume  $v_i$ , Boyle's law would hold, and

$$\frac{p_i}{p_b} = \frac{v_f}{v_i} \quad (3)$$



We may then substitute  $\frac{p_i}{p_b}$  for  $\frac{v_f}{v_i}$  in Equation 2, and get

$$\frac{p_i}{p_f} = \left( \frac{p_i}{p_b} \right)^\gamma.$$

Taking logarithms, we have

$$\log \frac{p_i}{p_f} = \gamma \log \frac{p_i}{p_b}$$

and

$$\gamma = \frac{\log p_i - \log p_f}{\log p_i - \log p_b}.$$

Sometimes this relationship is given in the form of an *approximate* equation,

$$\gamma = p_1/(p_1 - p_2), \quad \text{where} \quad p_1 = p_i - p_f; \quad \text{and} \quad p_2 = p_b - p_f;$$

e.g., see Getman and Daniels.

In this method for the experimental determination of  $\gamma$ , what are the principal sources of error? Compare its accuracy with that of the Kundt method.

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Taylor, Chap. III.

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Findlay, Chap. II.

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Edser.

Lewis and Randall.



## EXPERIMENT 5

### THERMAL CONDUCTIVITY OF GASES

Heat can be transferred through a gas by radiation, convection and conduction. At present we are interested in conduction alone. In the process of conduction kinetic energy is transferred by energy-rich molecules moving down a temperature gradient, from a hot to a cooler region of the gas, and by energy-poor molecules moving in the opposite direction. The specific thermal conduction, or the thermal conductivity, of a substance is defined as the time rate of transfer (by conduction) of heat across unit area through unit thickness for unit difference in temperature. The same thing may be said in terms of the equation

$$\frac{\Delta Q}{\Delta t} = k \cdot A \frac{T_2 - T_1}{d}$$

where  $k$  is the thermal conductivity expressed in c.g.s. units, if  $\Delta Q$  the heat transferred is expressed in ergs,  $\Delta t$  in seconds,  $A$  the area in sq. cm.,  $T_2$  and  $T_1$  in  $^{\circ}\text{C}$ ., and  $d$  the distance of transfer in cm. The thermal conductivity, which is the proportionality constant  $k$  in this equation, has different and characteristic values for different gases. It is related to other gas kinetic properties such as diffusion coefficient and viscosity. For example it can be shown that

$$k = \epsilon \cdot \eta \cdot C_v$$

where  $\eta$  is the viscosity of the gas,  $C_v$  is molar heat at constant volume for the gas, and  $\epsilon$  is a proportionality constant, which itself is characteristic of the particular gas. It is also true that thermal conductivity, like viscosity is *independent of the gas pressure over a wide range*.

It is a somewhat difficult matter to measure the thermal conductivity of a gas accurately because of the intervention of radiation and convection. They both are responsible for part of the total heat transferred, and reliable corrections cannot be easily made for the part they play. Nevertheless, thermal conductivities can be measured approximately, and they have an im-



portant application in gas analysis by certain calibration procedures.

Obviously it would not generally be feasible to employ a cubical vessel of gas exactly 1 cm. along an edge, maintain two opposite sides at temperatures differing by 1° C., and measure the heat carried across it in 1 sec. But by constructing a cell in which two parts are kept at constant but different temperatures, one can use in it a gas whose thermal conductivity is already known, and thus determine the "cell constant," and then employ it to determine the thermal conductivity of other gases.

In the following experiment an electric current is used to heat a fine platinum wire stretched along the axis of a metal tube kept at a constant temperature by immersion in a thermostat. The resistance of the platinum wire varies with the temperature, but at a definite temperature it has a definite resistance. Conversely, if it has a definite resistance it is at a definite temperature. This is the principle underlying the platinum resistance thermometer. Different gases placed in the metal tube conduct heat at different rates. This means that in order to maintain the wire at the same temperature different amounts of electrical energy must be supplied. Hence the electric current used to maintain the wire at a definite temperature (i.e., definite resistance) must be different for different gases.

The heat liberated by an electric current  $i$  is given by the equation

$$q = J \cdot e \cdot i \cdot t, \quad \text{or} \quad q = J \cdot i^2 \cdot r \cdot t,$$

where  $e$  is the difference of potential between the two ends of the wire through which the current flows,  $i$  is the current,  $r$  the resistance,  $t$  the time and  $J$  is the constant of proportionality. (If  $q$  is expressed in calories,  $e$  in volts and  $i$  in amperes, then  $J = 0.239$ .)

When a stationary flow of heat has been attained, i.e., when the temperature of the wire has attained a constant value, the amount of heat given out per unit time to the thermostat must be equal to the amount of heat generated in the same time at the wire. This amount is directly proportional to the thermal conductivity of the gas between the wire and the metal tube, if we neglect radiation and convection. In tubes less than 1 cm. in diameter, convection is negligible. While the radiation correction



is appreciable we may neglect it in the present experiment. As shown above, it is also proportional to the square of the current which must be used to keep the temperature of the platinum wire at the same value for all the gases concerned.

Thus, if we assume the thermal conductivity  $k$  of dry air to be known, that of any other gas may be found by measuring the currents which will maintain the wire at the same temperature, first with air and then with the other gas in the cell. If  $k_{\text{gas}}$  be the thermal conductivity of the gas, then  $k_{\text{gas}} = k_{\text{air}} \times i_{\text{gas}}^2 / i_{\text{air}}^2$ . Since in any one experiment the temperature, and therefore the resistance, of the wire is kept constant, the only quantity that need be measured is the current  $i$ .

### EXPERIMENTAL

Construct, or obtain from the instructor, a cell such as is shown in Fig. 12. It consists of a brass or copper tube about 10 to 20 cm.

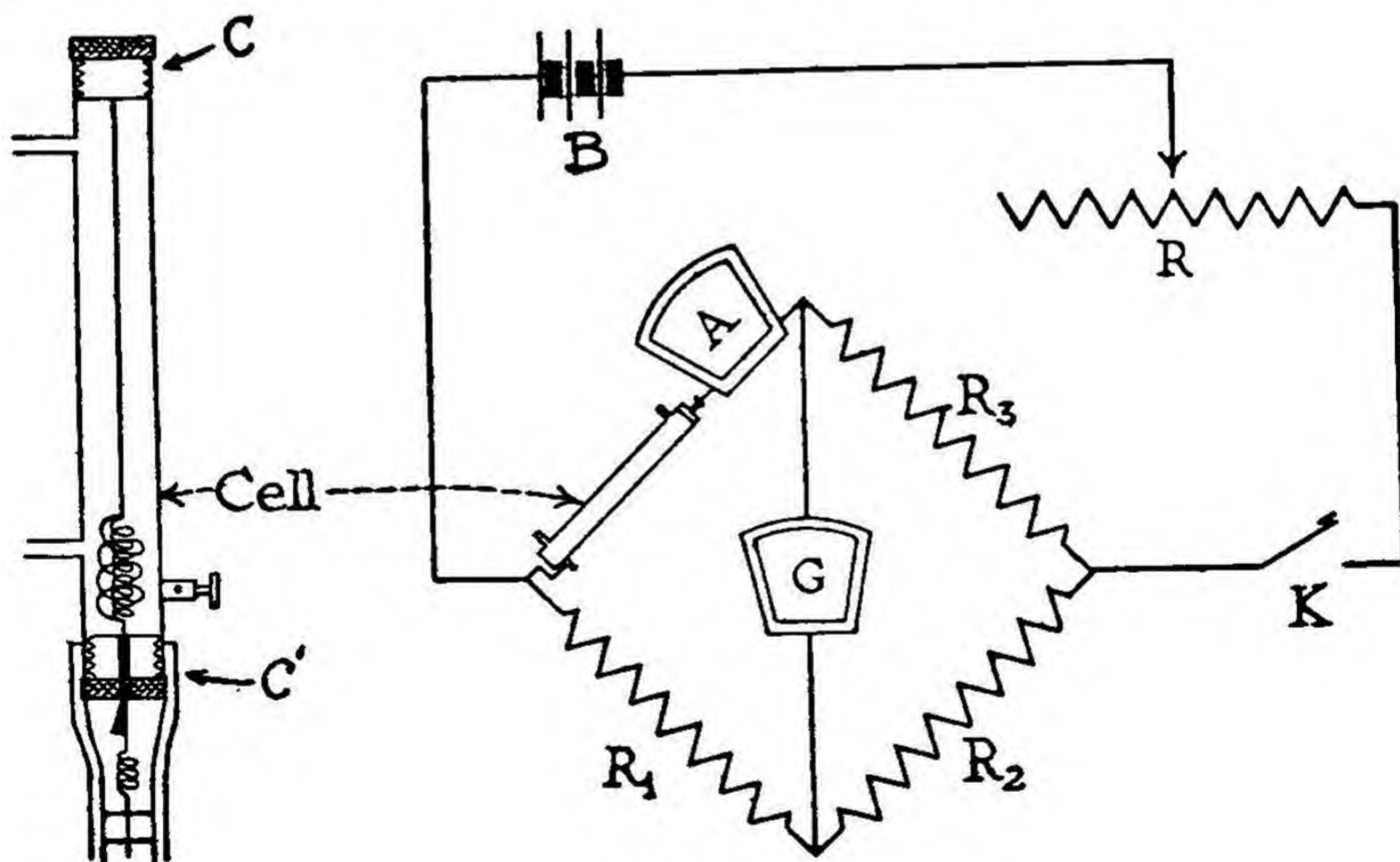


FIG. 12

long and of an internal diameter of from 6 to 10 mm., provided with a gas inlet at one end and an outlet at the other formed from smaller tubes soldered to the main tube. Old cork borers serve admirably for this purpose. The platinum wire, which should be as fine as is available, say from 0.03 to 0.1 mm., is fastened at one



end to a short length of fairly heavy (B. & S., No. 18 or 16) copper wire and soldered or clamped to the *metal* cap C which screws into the end of the tube. The most convenient method of fastening the platinum to the copper wire is to heat the end of the latter in a small blast-lamp flame until a drop of melted copper is formed and then insert the end of the platinum wire in the molten copper. The other end of the platinum wire is fastened to two wires, either by soldering, or by forming a fused drop, as above: one of these is a spring made of chromel wire B. & S. gage No. 28 or 30; its function is to keep the platinum wire drawn taut when it expands during heating. The other wire is a much looser coil of No. 26 or 28 copper wire; its function is to by-pass the current around the chromel spring to dodge the high electrical resistance of the latter. This copper wire is fastened to both ends of the spring, as indicated in the figure. It serves as one of the lead-wires, and runs out through, and is wedged tightly into, a small centrally drilled hole in the insulating cap C'. This wire continues on through the cap C' and is soldered to a heavy piece of No. 18 copper wire which serves as a more rugged lead-wire, and itself passes through a tight fitting rubber or cork plug inserted in a large piece of rubber tubing. The rubber tubing is forced over the end of the conductivity tube, as shown in the figure, and insulates the lead-wire from the thermostat bath. A binding post soldered to the outside wall of the tube serves as the other lead, and completes the cell. Care should be taken that the platinum wire is straight and is centrally placed along the axis of the tube.

When the cell is used, it is connected in a Wheatstone bridge arrangement as is shown by Fig. 12, where  $R_1$  and  $R_2$  are two variable resistances, preferably of the dial box type, and  $R_3$  is a large coil of copper having a resistance of 1 ohm (about 166 ft. of No. 18 copper wire) or less.  $R_3$  is made up in this way rather than using a resistance box like  $R_1$  and  $R_2$  in order to eliminate the possibility of a change in its resistance by the heating effect of the current. The galvanometer G is permanently connected as shown, the desk type manufactured by Leeds and Northrup being highly satisfactory. The resistance R controls the current from the storage battery B and may consist of a slide wire rheostat of about 20 ohms and another slide wire rheostat of about 1 ohm connected in series for fine adjustments.



The outside of the cell is kept at a constant temperature by means of a thermostat. The cell is filled with dry air, the circuit is closed by means of the key K, and the rheostat is adjusted to give a current not greater than 1 amp. as read on the ammeter A (which should be as accurate and sensitive an instrument as is available), and having set  $R_1$  at a definite value,  $R_2$  is adjusted until the galvanometer shows no deflection. The current is then carefully noted. The process is repeated several times, each time using a different value for  $R_1$ .

The air is then displaced by the gas of unknown thermal conductivity and the measurements of current are repeated exactly as before except that the values of  $R_1$  and  $R_2$  are made the same as they had been for air and only the rheostat R is adjusted until the galvanometer again shows no deflection. From the data thus secured the thermal conductivity of the gas may be readily calculated, assuming that the thermal conductivity of dry air is given by (Schneider, *Ann. Physik*, 79, 201 (1926))

$$k_{\text{air}} = (5.923 + 0.000933 t) \times 10^{-6} \frac{\text{cal.}}{\text{cm. sec. deg.}}$$

where  $t$  is the mean temperature of the gas. For the purposes of this experiment the temperature of the thermostat may be taken as the mean temperature. The average of the values thus obtained should be taken as the thermal conductivity of the gas. Another source of error is the leakage of heat through the ends of the platinum wire by metallic conduction.

Using the above method measure the thermal conductivity of hydrogen, oxygen, carbon dioxide, illuminating gas and of several mixtures of carbon dioxide and hydrogen of known composition.

For the last part, mixtures of the two gases may be readily made by displacing a salt solution previously saturated with the gases in an inverted liter graduated cylinder. This is closed with a large two-hole stopper through one hole of which passes a long capillary glass tube reaching to the end of the cylinder and through the other hole of which passes a connection to a reservoir for adjusting the levels of the liquid. The reservoir may be conveniently made from a bottle whose bottom has been removed.

Plot the thermal conductivity of the gaseous mixtures against



their composition, expressed in volume percents, and indicate how this method might be used to determine the composition of gases. In such a calibration procedure would the errors introduced by radiation, convection, or other heat leaks, make any appreciable difference in the gas analysis? In the best actual practice this is not exactly the procedure which is generally followed, although the method used does depend upon the different thermal conductivities of the components of the gaseous mixtures. For further details the student is referred to Palmer and Weaver, *Bur. Standards, Tech. Papers*, No. 249, or to Weaver et al., *J. Ind. Eng. Chem.*, 12, 359, 894 (1920).

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Loeb's, *Kinetic Theory of Gases*, pp. 201-18.

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Lamson and Robins, *J. Pharmacology and Experimental Therapeutics*, 34, 325 (1928).



## EXPERIMENT 6

### HIGH VACUUM TECHNIQUE; MERCURY VAPOR PUMP; MCLEOD GAGE; VAPOR PRESSURE BY EFFUSION; PREPARATION OF POROUS COPPER MEMBRANE

With the experience which the student has already had in glass-blowing in Exercise IV, and with a little more practice and patience, it will not be difficult for him to construct a simple mercury vapor pump and a McLeod gage.

**Mercury Vapor Pump.** First look at Fig. 17(a) and (b), to see the form of the finished pump. Mercury vapor, coming from the liquid mercury heated in flask F, passes up the long tube T and sprays out of jet J into condenser S (water cooled), condenses and returns by gravity to flask F. When an oil pump, or other "fore-pump," capable of producing a vacuum of about 0.1 mm. is attached to the outlet P, the spray of mercury vapor issuing from jet J will knock air or other gas molecules along ahead of it, and produce an exceedingly good vacuum in a closed vessel attached to inlet L'.

The mercury vapor pump is to be constructed out of *pyrex* glass. A large tube, 25–30 mm. inside diameter, and about 25 cm. long, is drawn out (use a mixture of oxygen and air in gas flame)

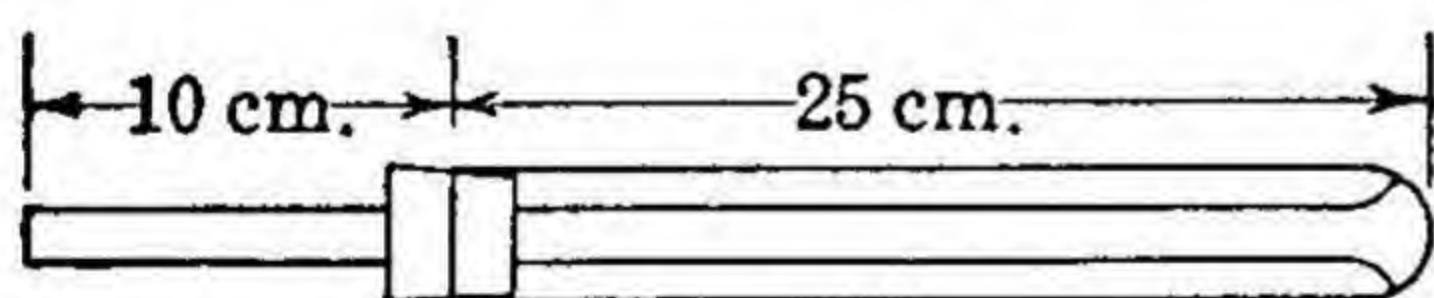


FIG. 13

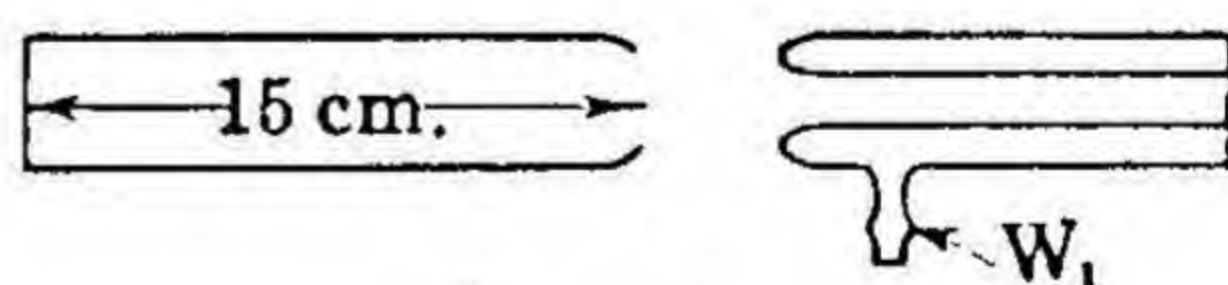


FIG. 14

and rounded up into test tube shape, at one end. A cork to fit the open end of this tube is bored to hold the inner tube of the condenser, about 12 mm. inside diameter. The latter should then be flanged to about 15 mm. at one end and inserted so that its lip rests on the curved portion of the closed bottom of the outer tube, as shown in Fig. 13. The inner tube should be about 10 cm. longer than the outer tube. If desired, the inner tube may be constricted at several points into a series of bulbs, S, Fig. 17.



This produces a slight injector action as well as a turbulent flow, and increases the rate of condensation in the completed pump.

Next, a side tube (water tube  $W_1$  in Fig. 17a) is added to the outer condenser jacket, as near the end as is possible, without deforming the flanged inner tube. The inner and outer tubes are then sealed together at the flange, by warming evenly the whole rounded end. A tube about 15 cm. long (which is eventually to carry the tube  $L'$ , Fig. 17) and of approximately the same diameter as the outer jacket is constricted slightly (this is best done by closing one end and blowing a hole of the desired size in it) so as to match the flanged end of the inner tube. At this point, the closed end of the inner and outer tube, previously sealed together, is blown out completely, the excess glass trimmed off, and while the end is still hot the large constricted tube should be sealed on, Fig. 14.

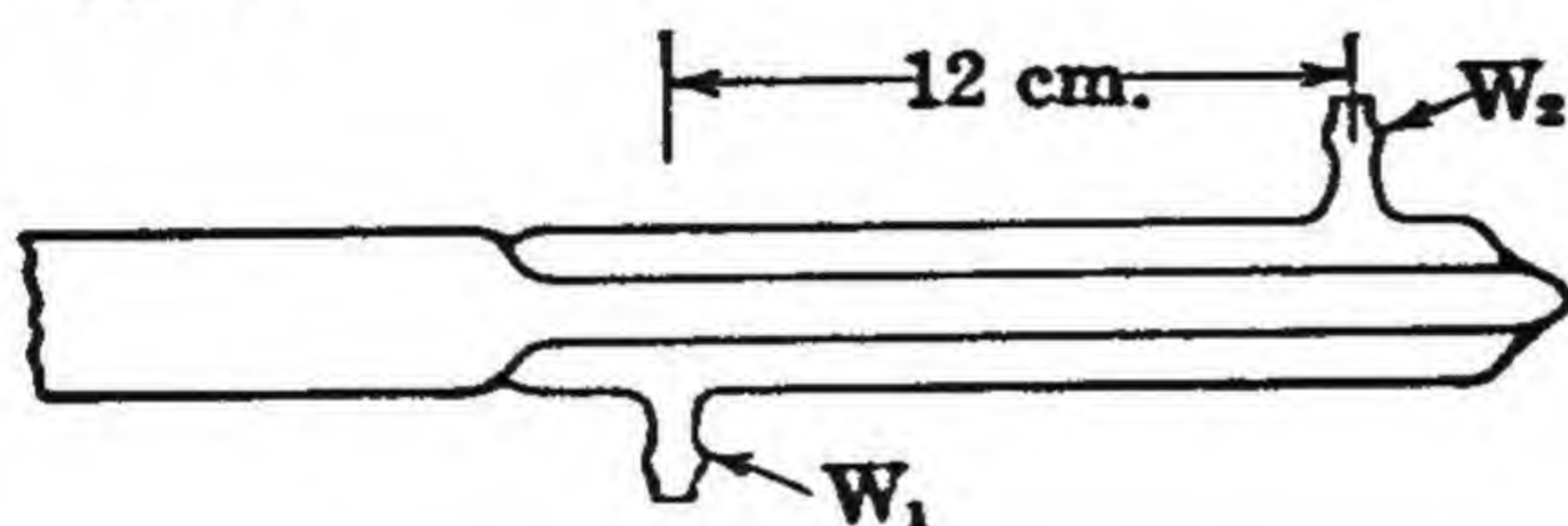


FIG. 15

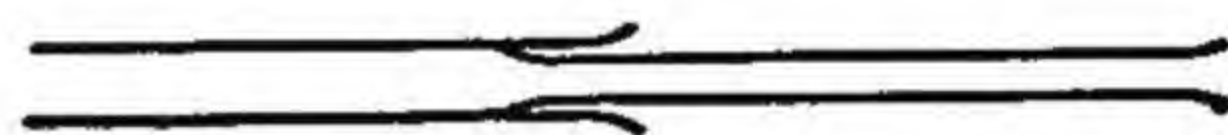


FIG. 16

The water tube  $W_2$  is next sealed on the condenser jacket at a point about 12 cm. from the tube  $W_1$  and on the opposite side. The remaining open end of the condenser is closed by sagging the outer tube on to the inner one and pulling both off together. Thus far the job resembles the form shown in Fig. 15. This seal is then rounded off, blown out and to it, while still hot, is sealed a tube (which is eventually to carry  $P$ ) of the same bore as the inner tube of the condenser.

The large tube at the upper end of the condenser is next sealed off at a point about 5 cm. above the inner seal and a hole about 16 mm. in diameter is blown in the closed end. A tube approximately 12 mm., inside diameter, is flanged to fit this opening. The jet tube, which should be 3 to 4 mm. smaller than the inner tube of the condenser is flanged to fit the inside of the 12 mm. tube and is sealed inside it at a point 1-2 cm. above the flanged end (Fig. 16).

The jet tube should extend about 2 cm. below the side tube  $W_1$



of the condenser. The efficiency of the pump is increased if the jet tube is flanged slightly at its lower end. It is important that the jet be square on the end and well centered. The tube holding the jet is sealed to the large tube above the condenser. The jet may be centered by softening this seal and working the jet to position.

The lead tube,  $L'$ , to the vacuum line is sealed on midway between the inner seal holding the jet and the upper end of the condenser. The tube,  $P$ , leading to the oil pump is sealed on just below the condenser and the pump is then completed as shown in the figure. A 50 cc. pyrex distilling flask may conveniently be used for the bulb.

The long vertical tube  $T$  should be insulated in some way, by wrapping it with a layer of asbestos rope, or by plastering over it a plastic paste of shredded asbestos and water glass, and allowing this to "set." The mercury flask may be heated electrically or with a small gas flame. A fairly rapid stream of cold water should flow through the condenser, in at  $W_2$  and out at  $W_1$ .

**McLeod Gage.** Figure 17 shows the arrangement of the mercury vapor pump, the McLeod gage and the large pyrex tube  $LL$ ,

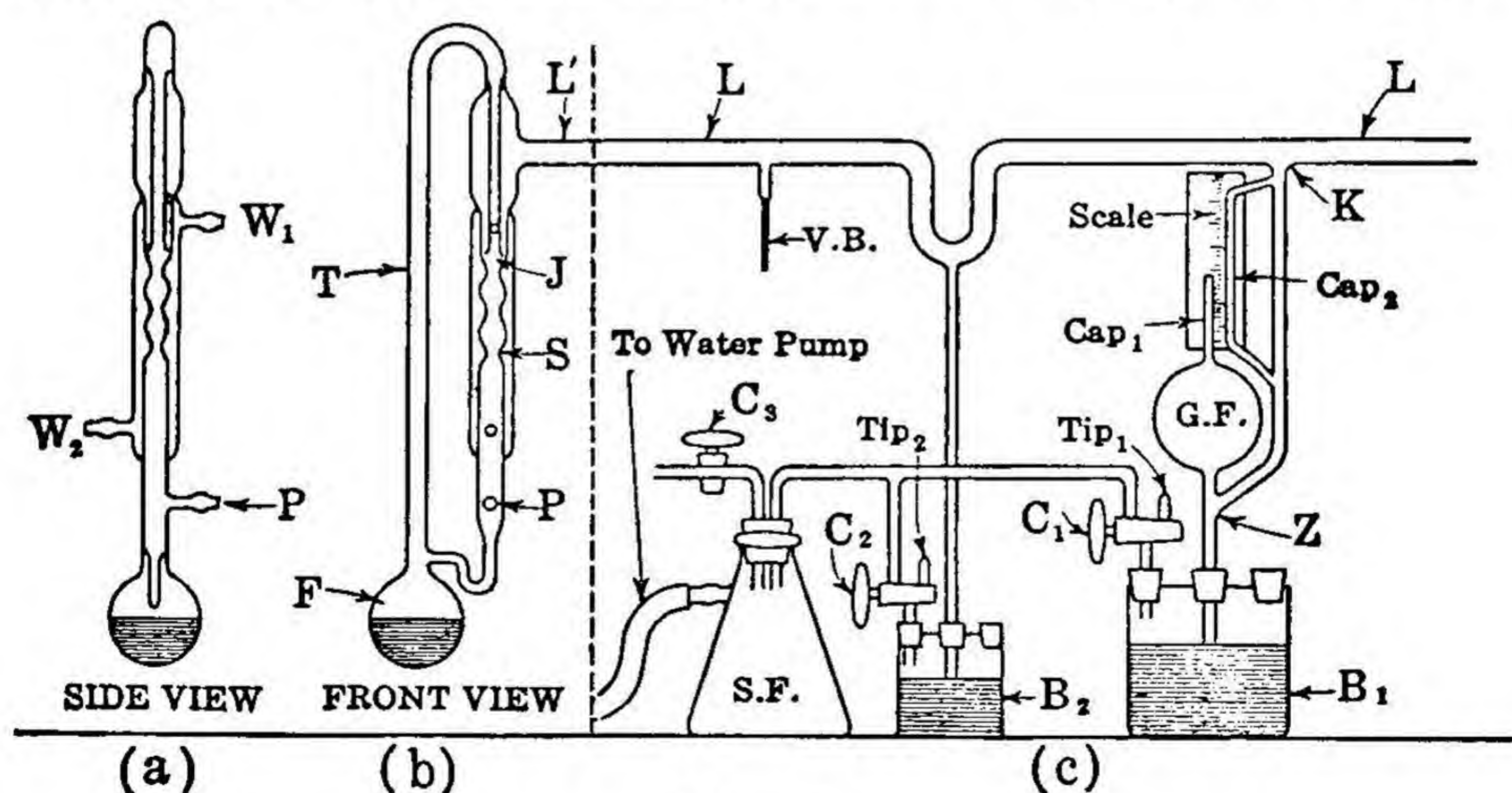


FIG. 17

leading to the system to be evacuated. The McLeod gage may be made either of pyrex or soft glass. In the former case it is sealed directly on to  $LL$  at  $K$ . In the latter case the soft glass is sealed to a pyrex side arm at  $K$  with de Khotinskiv or other cement.



The exact dimensions of the gage and its various parts will not be given, nor are they important. Figure 17(c) is drawn roughly to scale, and dimensions of this apparatus may be varied considerably depending on the purpose in view.

The gage itself is made of a 100–200 cc. flask, G.F., to the top of which is sealed a capillary,  $\text{Cap}_1$ , which is closed at the upper end. This capillary may be 1 mm. or less in inside diameter, and in the case of soft glass, it may be conveniently made from a graduated capillary pipette tube. Otherwise, if made from pyrex, the capillary must be marked off by etching volume divisions, of say cubic mm., throughout its entire length, unless of course a pyrex capillary pipette is available. The calibration of the volume intervals, etched on the capillary, should be accomplished by filling to several of the marks with mercury and weighing, before sealing the capillary to G.F. To the lower end of G.F. is sealed a vertical tube, 7–8 mm. inside diameter, leading down into a well of mercury in the 3-neck Wolff bottle  $B_1$ . Sealed on to this tube at Z is a side-arm tube of similar diameter, leading up to K; and sealed into the side-arm tube at two places, as shown in the figure, is a capillary tube,  $\text{Cap}_2$ , of the same diameter as  $\text{Cap}_1$ . One of the necks of bottle  $B_1$  is sealed with a rubber stopper securely seated in place, and in the other neck is fastened a rubber stopper bearing a 3-way stop-cock  $C_1$ . One arm of this cock is drawn to a fine tip, which opens to the air,  $\text{Tip}_1$  in the figure. The other arm is connected to the suction flask S.F., which in turn is connected to a water pump (not shown in figure). The total volume of  $\text{Cap}_1$  and of G.F. down to Z must be known, and can be determined by filling with mercury and weighing before the assembly of the apparatus. Let us call this volume  $V$ .

The gage functions as follows. When the connecting tube LL is sealed at  $L'$  to the mercury vapor pump, and is either closed hermetically at the right-hand end, or is sealed to a closed system which is to be evacuated, and when a fore-pump is connected to P, and the mercury pump has begun to operate, a good vacuum will soon be created in LL, and also of course in G.F. and in the other portions of the gage. In fact the pressure in the gage will be the same as in LL. To prevent the mercury in  $B_1$  from being drawn up into G.F. before we are ready for it, stop-cock  $C_1$  is opened to the water pump (with stop-cock  $C_2$  closed). Then, when the mo-



ment has come to measure the gas pressure in LL, stop-cock  $C_1$  is turned to  $Tip_1$  and air slowly enters  $B_1$ , forcing mercury up the tube. At Z the mercury column divides, part of it going up into G.F. and trapping off a volume of gas (air) equal to  $V$ , referred to above. This gas is compressed, as the mercury piston continues to rise, until finally all of the air has been pushed into the capillary  $Cap_1$ . The pressure of this compressed volume of air (in  $Cap_1$ ) can now be obtained by measuring, on the millimeter scale, the difference in level between the mercury in  $Cap_1$  and  $Cap_2$ , because in the meantime, the other mercury column, which divided at Z, has risen in the side arm and in  $Cap_2$ , and the air above these columns of mercury is *not* compressed, but has the pressure of the vacuum which the mercury pump is maintaining.  $Cap_2$  is made the same size as  $Cap_1$  and the pressure reading is between the mercury levels in  $Cap_1$  and  $Cap_2$ , rather than between  $Cap_1$  and the larger side-arm, to avoid the capillary depression correction.

We can calculate the pressure in the gage at the time that the air is trapped off at Z by using Boyle's law:  $P/p = v/V$ , where  $P$  = original pressure (to be calculated),  $p$  = pressure in  $Cap_1$ ,  $v$  = volume of air in  $Cap_1$ , and  $V$  = total volume of G.F. The sensitivity of the gage depends on the sizes of G.F. and  $Cap_1$ . With the dimensions suggested above, the gage can easily be read to  $10^{-5}$  mm., and estimated to  $10^{-6}$ . The presence of mercury vapor in the gage does not interfere with its action, since this vapor is condensed out on the liquid mercury surface as the air is compressed. At room temperature mercury has a vapor pressure of only about 0.001 mm. At the completion of the determination the mercury in G.F. can be made to drain back into  $B_1$  by opening stop-cock  $C_1$  to the water pump. The pressure of vapors and easily condensable gases cannot be measured satisfactorily with a McLeod gage. The vacuum may be conveniently broken by scratching the fine drawn-out tube V.B. with a file, breaking it off near the tip and placing a finger over the hole to regulate the intake of air. Then the tube is to be repaired, of course, by sealing it again.

An added feature of the apparatus, which is often convenient although not at all necessary, is the large U-tube mercury seal, shown just to the left of the gage in the figure. If stop-cock  $C_2$  is turned to the water pump the mercury is kept in the well  $B_2$ ; but if



C<sub>2</sub> is opened to the air through Tip<sub>2</sub>, mercury may be made to rise up into the U-tube and shut off the mercury vapor pump from the rest of the apparatus.

Such a mercury vapor pump, if correctly made and properly operated, will quickly produce a vacuum of  $10^{-4}$  to  $10^{-5}$  mm. It is not necessary to make the mercury in flask F boil violently; a gentle evaporation suffices. It is best not to heat it at all until the fore-pump is working. Theoretically, there is really no limit to the degree of vacuum which can be obtained. In practice, however, gases and water vapor, adsorbed on the inside glass walls and dissolved in the glass, slowly escape and spoil the vacuum to a slight extent. It is absolutely necessary of course to stop up all leaks. Tiny pin-hole leaks are especially likely to be found around the glass joints in the apparatus. A good way to locate these is to connect one end of the secondary of an induction coil to a piece of wire (tungsten in the case of pyrex, and platinum in the case of soft glass) sealed through the apparatus wall at some convenient point, and then to probe around with the other end of the secondary (should be tied to the end of a long glass rod handle to insulate it from the hand of the operator). An easily observable spark will jump to any leak-holes. Or one of the usual leak testers, which operate on the induction coil principle, may be employed.

Finally, since mercury vapor is omnipresent in such an apparatus as that shown in Fig. 17, it should be pointed out that if one wishes for any reason to prevent the entrance of mercury vapor into the system to be evacuated, attached to the right-hand end of LL, it will be necessary to insert a glass trap, immersed in liquid air or in a dry ice — acetone mush, to condense the mercury, and thus stop its penetration. Such a trap is shown below in Fig. 18. Recently, to avoid the necessity for such a trap, certain very non-volatile organic liquids, such as butyl-phthalate, with vapor pressures only about 1/1000 that of mercury, have been substituted for mercury in the pump, with a good deal of success. The jet J must be very carefully made, however, for these substances, and is probably more satisfactory when constructed of metal. (See Hickman and Sandford, *Rev. Sci. Instruments*, 1, 140 (1930); Estermann and Byck, *ibid.*, 3, 482 (1932). In such a set-up without a mercury vapor trap, however, the McLeod gage



which involves the use of mercury, must be omitted. Other types of gages may be used.

The fundamental purpose of these directions for the construction and manipulation of a mercury vapor pump and a McLeod gage is to acquaint the student with the details of this powerful technique, and to encourage him to acquire some skill in its use. There are numerous interesting things which can be done with such an apparatus. We shall now suggest only two experiments, which the student may or may not care to perform, to illustrate partially the possible applications of this high vacuum technique.

**Vapor Pressure by an Effusion Method.** Construct out of glass, preferably pyrex, the apparatus shown in Fig. 18; or obtain it from the instructor. A trap *T*, later to be immersed in liquid air or a mush of dry ice and acetone contained in a thermos bottle or Dewar tube, is sealed to LL in Fig. 17, leading to the mercury-vapor pump and McLeod gage. To the other end of the trap is sealed a tube of the indicated form. To the large open end of this tube *F* a brass form *B* is attached, with a hermetical seal, using picein, or beeswax or paraffin. This form *B* may easily be turned out on a lathe from a solid cylindrical piece of brass about 3 to 4 cm. in diameter. Fitting inside the form *B* is a pill box *H*, also made of brass, 2.5 to 3 cm. diameter, with a brass lid which screws on tightly enough to be leak-proof, or can be made so by using lead bushings. A hole about 5 mm. in diameter is drilled in this lid, and a piece of thin brass or copper or platinum foil is soldered over it. Then a small hole about 0.5 to 1 mm. diameter is punched in the foil with a needle, and the ragged edges are removed. The area of this hole is measured in a microscope provided with a calibrated scale in the eyepiece.

The procedure involves determining the weight of a somewhat volatile substance, like aniline or naphthaline, lost by effusion out of the pill box through the hole into the vacuum in a known

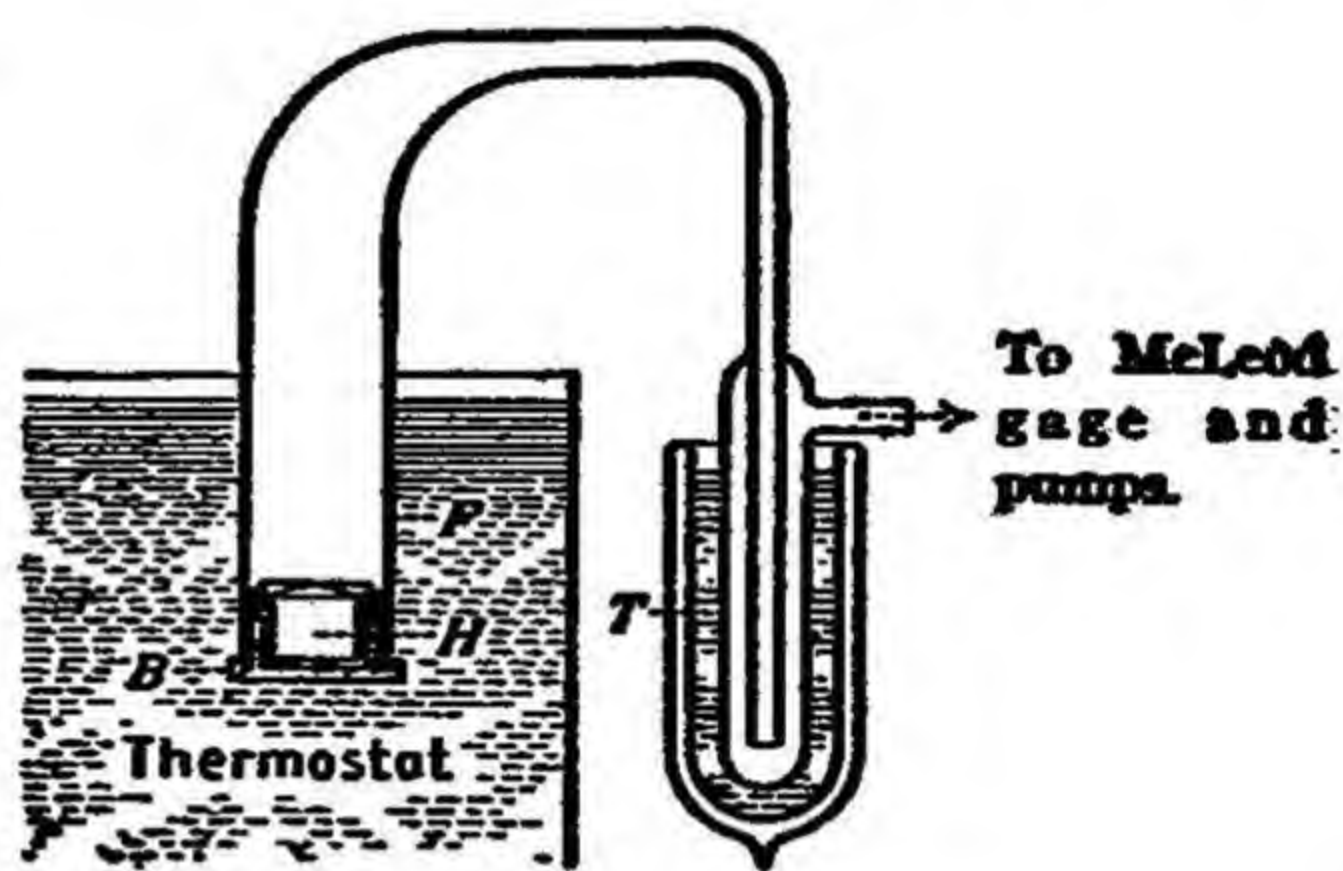


FIG. 18



time. Naphthalene is a good working substance. Obtain a sample of pure naphthalene, introduce some of it into the pill box, melt it and allow it to cool and solidify, so that the bottom of the box is covered to a depth of not more than about 1 mm. Screw on the lid tightly and weigh to 0.1 mg. Slip pill box into form B, and with as little warming as possible, seal form B to the glass tube with wax so that there are no leaks. Then immerse it in a large beaker of water hand-regulated to 25° C. Introduce the trap into the liquid air or dry ice mush, and turn on the mercury vapor pump, which should previously have been made ready for instant use by a preliminary warming up of the mercury. Start counting time on a watch at once and let the effusion continue for about an hour of measured time, at a pressure, measured on the McLeod gage, at least as small as  $10^{-4}$  mm. If it is as small as this it will make no difference how much smaller it may be. Then stop the pumps (at the end of an hour). Break the vacuum at V.B. Fig. 17. Remove form B and again weigh the pill-box. The determination should then be repeated, but for only about half an hour. By subtracting the loss in half an hour from the loss during the full hour, obtain the true loss during half an hour, with correction automatically made for the uncertainty about just exactly when the good vacuum takes hold during the first few minutes of the run.

Assuming that the pill box is saturated with the naphthalene vapor throughout the determination, and that the thermal conductivity of the naphthalene layer is sufficiently good to maintain it constantly at the thermostat temperature, calculate the vapor pressure,  $p$ , of the naphthalene, using c.g.s. units, and finally converting the answer to mm. of mercury, from the following equation (see Rodebush, p. 22),

$$p = \frac{g}{A \cdot t} \sqrt{\frac{M}{2 \pi R T}}$$

where  $g$  = grams lost by effusion,  $A$  = area of hole,  $t$  = time,  $M$  = molecular weight,  $R$  = gas constant and  $T$  = absolute temperature of thermostat. This equation holds strictly only when the walls of the evacuated glass tube are very remote from the effusion hole, or when the walls are made so cold that all of the vapor molecules which strike them condense and do not evaporate



again, or at least have no chance to be reflected back into the pill box through the effusion hole. In the set-up described above, the effusion hole is so small compared with the diameter of the glass vessel that no appreciable error (less than 1%) occurs due to the re-entry of vapor molecules through the effusion hole. To be successful this determination must be carried out with a vacuum good enough (about  $10^{-4}$  mm.) to make the mean free path of the vapor molecules, after they escape from the effusion hole, very long. The student may consult *J. Am. Chem. Soc.*, 47, 2115 (1925), for comparison data on vapor pressure of naphthalene.

**Preparation of Porous Copper Membrane.** Cut out a piece, about as big as a postage stamp, of very thin "shim" brass, about 0.001" thick, such as is used in bushing automobile bearings, and place it in a quartz test tube 2 to 2.5 cm. in diameter, the open end of which is then drawn down and sealed on to a quartz tube 8 to 10 mm. in diameter and about 25 to 30 cm. long. This, in turn, is sealed on to the LL tube of the vacuum system in Fig. 17, either with a "quartz-pyrex seal," or by using de Khotinsky or other vacuum-tight cement. Heat the quartz test tube containing the brass foil in a small electric furnace at about  $600^{\circ}$  C. (a good red heat) for about 20 hours, with the vacuum pump operating at a pressure as low as  $10^{-4}$  cm., until all or nearly all of the zinc has been distilled out of the brass, as indicated by the deposition of zinc in the quartz tube just outside of the furnace. If a cement has been used to make the union to LL, it is well to keep the joint cool by directing a jet of air on it.

The copper foil which is left behind after the removal of the zinc (about 30–35% of the total weight of brass is zinc) is finely porous. Although no holes or porosity can be observed even with the most powerful microscopic observation, such a porous membrane will pass small gas molecules like  $N_2$ ,  $O_2$ ,  $CO_2$ ,  $CH_4$ , etc., but will stop large molecules like  $C_6H_5 \cdot CH_3$ ,  $C_2H_5 - O - C_2H_5$ , etc. This can readily be demonstrated by placing the copper membrane in a leak-tight holder between two leveling burettes, containing various gases, manipulated with mercury. The rate of transpiration can be shown to be directly proportional to the difference of pressure on the two sides of the membrane, thus proving that the flow of gas molecules through the pores of the



membrane is of the *molecular* type, rather than *viscous flow*, the latter being proportional to the difference of the *squares* of the pressures. This porous copper foil may also be used as an osmotic pressure membrane, between water and a cane sugar solution, for example; although the rate of osmotic flow is very small. For details, see *J. Am. Chem. Soc.*, 55, 1324 (1933).

REFERENCES:

Dushman, *High Vacuum*.

Du Noyer and Smith, *Vacuum Practice*, G. Bell & Sons.

Hoeg, *Electron Physics*.



## EXPERIMENT 7

### DETERMINATION OF THE VAPOR PRESSURE OF ACETIC ACID BY THE USE OF THE DUMAS BULB

**Directions.** Put a right angle bend in the tube of a Dumas bulb two inches from the end. Weigh empty, then fill with distilled water and weigh again. (The bulb is best filled in the following way. Fill an 800 cc. beaker half full of water, add about 50 grams of salt, and bring it to the boiling point. Immerse the bulb for one minute, withdraw and place tip under distilled water. When all has sucked in that will, heat bulb now partially filled with water in water-bath until steam has been generated in bulb for five minutes. Without any cooling immerse end of tube under distilled water.) Empty the bulb, dry inside, and introduce about 5 cc. of glacial acetic acid. Weigh again and place in a thermostat which consists of a 1-liter beaker  $\frac{2}{3}$  full of water, hand regulated to  $30^{\circ}\text{C.} \pm 0.5^{\circ}$ . After ten minutes read the barometer and put the end of the tube in a beaker of distilled water which has been cooled to  $0^{\circ}\text{C.}$  by a *salt-ice* mixture, and place the bulb in an *ice-water* mixture. When water has ceased to flow in, remove bulb and weigh again. When removing bulb, the thumb should be placed over the tube tip and the bulb should be slightly tilted until the water in the tube has drained into the bulb. Failure to do this will result in loss of some water due to spurting when the air in the flask expands upon warming. Weighing need only be to 0.1 gm. in each case. Repeat the experiment. (It is not necessary to repeat the weighing of the bulb full of water.)

**Principles Involved.** This experiment involves Dalton's Law of Partial Pressures. It is assumed that the bulb is filled with air and acetic acid vapor before cooling, and with air and water vapor only, after cooling. Knowing the barometric pressure and the partial pressure of the air the vapor pressure of acetic acid is determined by difference.

(Question. Why could not the vapor pressure of benzene be determined in this way?)



1. Condition at  $T_1 = (30^\circ \text{C.} \pm 0.5^\circ)$ :

$$(p_B - p_{\text{HAc}})V_1 = N_A RT_1. \quad (\text{a})$$

$p_B$  = barometric pressure.

$p_{\text{HAc}}$  = vapor pressure of acetic acid at  $T_1$ .

$V_1$  = volume occupied by gases at  $T_1$ .

= volume of bulb minus volume of HAc (Liquid).

$N_A$  = mols of air in flask at  $T_1$ .

$$T_1 = 30^\circ \text{C.} \pm 0.5^\circ = 303.2^\circ \text{K.} \pm 0.5^\circ.$$

2. Condition at  $T_0 = (0^\circ \text{C.})$ :

$$(p_B - p_W)V_0 = N_A RT_0. \quad (\text{b})$$

$p_B$  = barometric pressure.

$p_W$  = vapor pressure of water at  $0^\circ \text{C.} = 4.57 \text{ mm.}$

$V_0$  = volume occupied by gases at  $T_0$ .

$N_A$  = mols of air in flask at  $T_0$ , same number as at  $T_1$ .

$$T_0 = 0^\circ \text{C.} = 273.2^\circ \text{K.}$$

$$p_{\text{HAc}} = \frac{p_B \cdot V_1 - N_A RT_1}{V_1}, \text{ from (a).}$$

Substitute from Equation (b) for  $N_A$  to determine  $p_{\text{HAc}}$  in terms of experimental quantities.

#### REFERENCES:

Taylor, Chap. III.

Rodebush, Chap. II.

Getman and Daniels, Chap. VII.

Millard, Chap. II.

Findlay, Chap. II.



## EXPERIMENT 8

### VAPOR PRESSURE MEASUREMENT; A BOILING POINT METHOD

The vapor pressures of many liquids, and their vapor pressures as a function of temperature, can be determined with considerable accuracy by measuring their boiling points at various pressures (one of the so-called "dynamic" methods). The accuracy attainable is sufficient for most purposes, and indeed is all that is generally justified by the purity of the material, unless extreme measures have been taken to achieve exceptionally high purity.

#### EXPERIMENTAL — VAPOR PRESSURE OF WATER

Figure 19 shows the arrangement of the apparatus. Distilled water is placed in the boiling tube T, which is provided with a side arm cooled by a short condenser C (see Exp. 15 for a more convenient form of condenser), and is further connected with a mercury manometer M and to a large bottle S of 5–10 liters capacity. The manometer scale should be about 85 cm. long. S is connected to a good water pump through the stop-cock A by means of which the system may be isolated from the pump. By regulating the flow of water in the pump, and by letting more or less air leak in through stop-cock B, the pressure in the system can be adjusted and controlled within quite narrow limits. The reservoir of air in bottle S helps to smooth out any small irregularities of pressure in the system, and in addition the bottle serves as a trap in case any water is accidentally

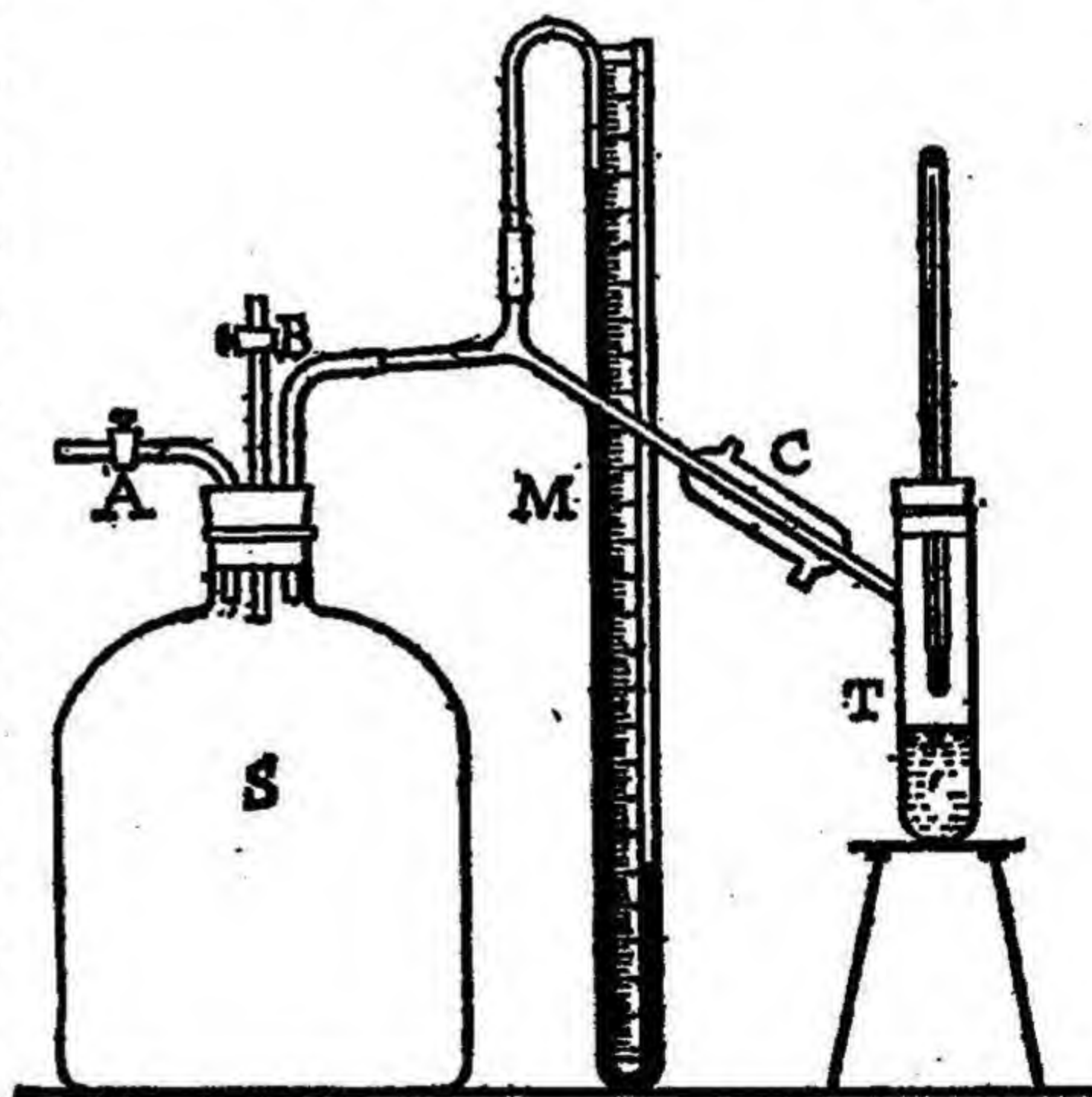


FIG. 19



sucked over from the pump. *The bottle should be encased in a jacket made of heavy cloth to catch the flying glass in case the bottle collapses.*

The water is heated with a small flame (micro-burner), the pressure is adjusted, and the thermometer and manometer readings taken as the water just begins to boil. Because of possible variations in the size of the glass tubing, both levels in the manometer should be read. Little difficulty should be encountered in obtaining constant temperature and pressure readings when working near atmospheric pressure, that is, with small difference in level between the mercury columns in the two manometer arms. But at low pressures, especially in the region 30–45 mm., which is about the lower working limit, three difficulties develop, (1) bumping, (2) pressure fluctuations, (3) temperature fluctuations. If (1) and (2) can be avoided, (3) tends to disappear. Bumping not only causes temperature fluctuations but may force most of the water in the boiling tube over into bottle S. Bumping may be largely prevented by adding small bits of porous plate, or large-sized ebullator tubes. It will be found that pressure fluctuations occur unless the suction pump is given careful attention. The stop-cock A may be closed, thus disconnecting the system from the pump, and thus constant pressure can be maintained for each reading. But in order to do this all the connections in the apparatus must be covered with shellac and made completely air-tight. If the mercury manometer columns fluctuate up and down unavoidably, due to bumping, take the average position of the column, as nearly as it can be estimated, as the correct reading.

Boiling point readings should be obtained for at least ten different pressures, starting at low pressure by pumping down as low as possible with the water pump first, and then breaking the partial vacuum, by manipulating stop-cock B, and letting the temperature rise. Half of the readings should be above 400 mm. and half below. The bulb expansion error introduced because the thermometer is read when its bulb is in a partial vacuum rather than at atmospheric pressure lies within the experimental error and may be neglected. The usual emergent stem correction should, however, be made. This may be estimated with the following equation

$$T_c = T_0 + 0.00016 l(T_0 - T_m)$$



where  $T_c$  is the corrected temperature,  $T_o$  the observed temperature,  $T_m$  the average temperature of the emergent mercury thread measured with another thermometer,  $l$  the length in degrees of the emergent thread, and 0.00016 is the apparent coefficient of expansion of mercury in glass, that is, it is the difference between the coefficients of expansion of mercury and glass.

Plot a curve, making your observed pressures the ordinates and corrected temperatures the abscissas, on an *extra large* piece of co-ordinate paper, and on the same sheet for comparison plot the vapor pressure data for water given in the Landolt-Börnstein Tables or in other tables of data.

### CALCULATION OF HEAT OF VAPORIZATION

Using the Boltzmann factor treatment for this situation we get

$$\frac{n_v}{n_l} = e^{-\frac{\lambda}{RT}}$$

where  $n_v$  and  $n_l$  are the numbers of molecules per cc. in the vapor and in the liquid, and  $\lambda$  is the total work required to transfer a mol from the liquid to the gaseous state. Since  $n_l$  changes only slightly with changing temperature, we may write  $n_v/n_l = p/C$ , where  $p$  represents the vapor pressure, i.e. the pressure of the saturated vapor, and  $C$  is a constant. Hence

$$\frac{p}{C} = e^{-\frac{\lambda}{RT}}.$$

Taking logarithms, we get

$$\ln p = -\frac{\lambda}{RT} + \ln C, \quad \text{or} \quad \left( \log p = -\frac{\lambda}{2.3 RT} + \log C \right). \quad (1)$$

To determine the rate of variation of  $\ln p$  with changing temperature, let us differentiate with respect to  $T$ :

$$\frac{d \ln p}{dT} = \frac{\lambda}{RT^2}. \quad (2)$$

This is the Clapeyron-Clausius equation.

Several different methods may be employed to calculate the heat of vaporization from the vapor pressure data. If the Clapey-



ron-Clausius equation be integrated and the natural logarithms converted to logarithms to base 10,

$$\log p_2 - \log p_1 = \frac{\lambda}{2.3 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2)$$

the values of the vapor pressures at two temperatures not too far apart may be inserted and  $\lambda$ , the molar heat of vaporization, calculated. However, this equation is integrated on the assumption that  $\lambda$  is independent of temperature, and while this is approximately true for some liquids (and solids), it is not true for water. Even if the two temperatures selected are rather close together, this method of calculation gives only an approximation to the average value of  $\lambda$  over the temperature interval.

An easy graphical test of whether or not  $\lambda$  for a certain substance is independent of temperature may be made by plotting the logarithms of the pressures against the reciprocals of the absolute temperatures. If a straight line results,  $\lambda$  is constant. The slope of the line is  $\frac{-\lambda}{2.3 R}$  (see Equation 1) and  $\lambda$  may be determined graphically.

In the case of substances, such as water, for which a plot of this sort does not give a straight line, it is best to find an empirical equation which expresses vapor pressure as a function of temperature. By evaluation of the constants  $A$ ,  $B$  and  $C$ , an equation of the form

$$\log p \text{ (in mm.)} = \frac{A}{T} + B \log T + C$$

can be made to fit the vapor pressure data for a very large number of substances. It serves very well for water. To evaluate the constants, set up three equations of this sort. In the first substitute your measured value for the vapor pressure of water not far below  $100^\circ$ , in the second at  $60^\circ$ – $70^\circ$ , and in the third a pressure found at one of the lowest temperatures. It is best to select data from the smooth curve, plot of vapor pressure against temperature on the large piece of graph paper. Solve these three simultaneous equations for  $A$ ,  $B$  and  $C$ . Calculate the heat of vaporization at  $50^\circ \text{ C.}$  by differentiating the terms of the equation with respect to  $T$ , inserting the value of  $T$ , and substituting for  $\frac{d \ln p}{dT}$  in



Equation 2. Compare your result with the value given in standard tables for the heat of vaporization of water.

One disadvantage of the method just described is that the data selected for substitution in the empirical equation in the evaluation of the constants may not be representative data. One can generally be guided, however, in the selection of the data by the manner in which the plotted points fall along the smooth curve. After the empirical equation has been found, it should be used to predict a number of points along the curve, as a test of whether the equation really expresses the data within the limits of experimental error.

In the plot of vapor pressure against temperature a graphical determination of the tangent or slope  $\frac{dp}{dT}$  of the curve at any temperature point permits a calculation of  $\lambda$  to be made, since Equation 2 can be written in the form

$$\frac{dp}{dT} = \frac{\lambda \cdot p}{RT^2}.$$

Recently a clever device known as a "tangentiometer" has been described by Latshaw (*J. Am. Chem. Soc.*, 47, 793 (1925)) for drawing the tangent to a curve at any point. It consists of a steel square B with a mirror mounted on one leg, so that the reflecting surface, either of polished speculum metal or a thin glass mirror, is at A, and is mounted so as to be normal to the edge ab (Fig. 20). "When the mirror is standing across a given curve, and is normal to it, there will be no break between the curve and its image at the foot of the mirror; any deviation from the normal will cause a noticeable break. Obviously, then, the line ab will be parallel to the tangent at that point, and the numerical value of the tangent can be obtained from its intersection with the abscissas and ordinates of the paper on which the graph is plotted."

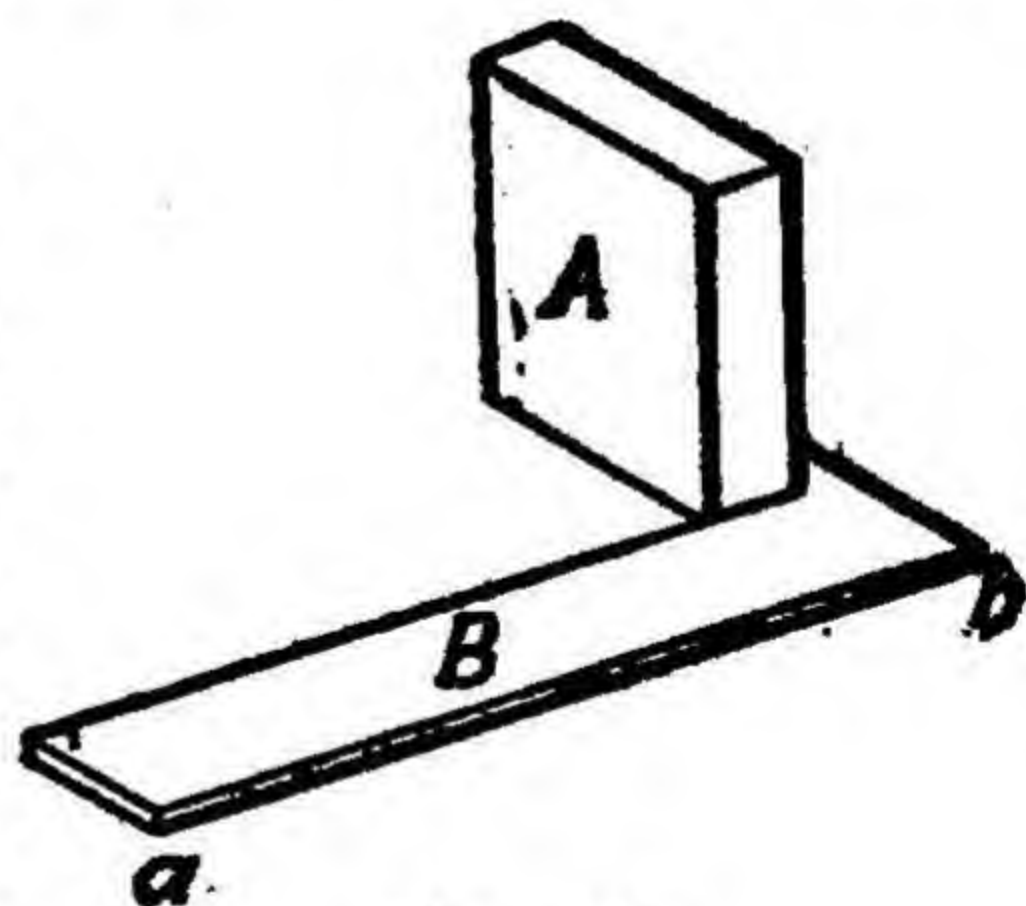


FIG. 20

Calculate the heat of vaporization from the slope, making use of a tangentiometer, or any graphical or other method for determining



tangents, and compare with the result obtained by the empirical equation method.

**Note on Bumping.** The boiling point of a liquid may be defined as the temperature at which bubbles form in the interior of the liquid. If these bubbles are formed and if they are to grow in size, the pressure of the vapor inside the bubbles must be a little greater than the combined pressure of the atmosphere and the hydrostatic pressure of the liquid. As the bubble grows, the surface tension of the bubble film must also be overcome. It can be shown thermodynamically as well as experimentally that the vapor pressure of a liquid at a concave surface, such as the inside surface of a bubble, is smaller than at a plane surface, and that the greater the degree of curvature of the surface, that is the smaller the bubble, the smaller will be the vapor pressure. Now when a liquid boils the bubbles must all pass initially through the stage of very small size, and it is precisely in this stage that the vapor pressure is abnormally low. Hence the temperature of the liquid must be raised above the true boiling point, and when the bubbles are produced they form with semi-explosive violence. If, however, ebullator tubes, or pieces of porous plate, or other inert materials be introduced, which give off air bubbles of relatively large size, the liquid can then evaporate at its normal vapor pressure through the comparatively flat surfaces of these bubbles. In a certain sense the liquid may be thought of as being slightly supersaturated with its own vapor, which is given off when seeded with bubble surfaces of small degree of curvature.

**REFERENCES:**

- Taylor, Chap. IV.
- Rodebush, Chaps. III and VI.
- Getman and Daniels, Chaps. III and VI.
- Millard, Chap. III.
- Findlay, Chap. IV.



## EXPERIMENT 9

### MEASUREMENT OF LIQUID DENSITY; HEAVY WATER; CONSTANT BOILING HCl; ETC.

In this chapter some of the standard methods for the measurement of the density of liquids will be briefly described, and at the end several suggestions for application of the technique, which the student may undertake with profit, will be made.

(1) Where no great accuracy is required, a set of the usual floating hydrometers, scaled for various ranges of density, may be conveniently used.

(2) Or, if it is required to determine the density to the 4th decimal place, 0.0001, the Mohr-Westphal balance, shown in Fig. 21, is satisfactory. This balance consists of a beam B supported on a knife edge K, and provided at the left-hand end with a counterpoise C, and a pointer which moves over a scale. At the right-hand end is a knife edge from which is suspended by a platinum wire a glass bob A. (Sometimes the thermometer, shown here clipped on to the side of the containing vessel, is incorporated in the bob.) The instrument is so arranged that when it is leveled with the screw L, and when the glass bob is hanging in air, the beam is perfectly balanced. If it is not, adjustment of the counterpoise C will make it so.

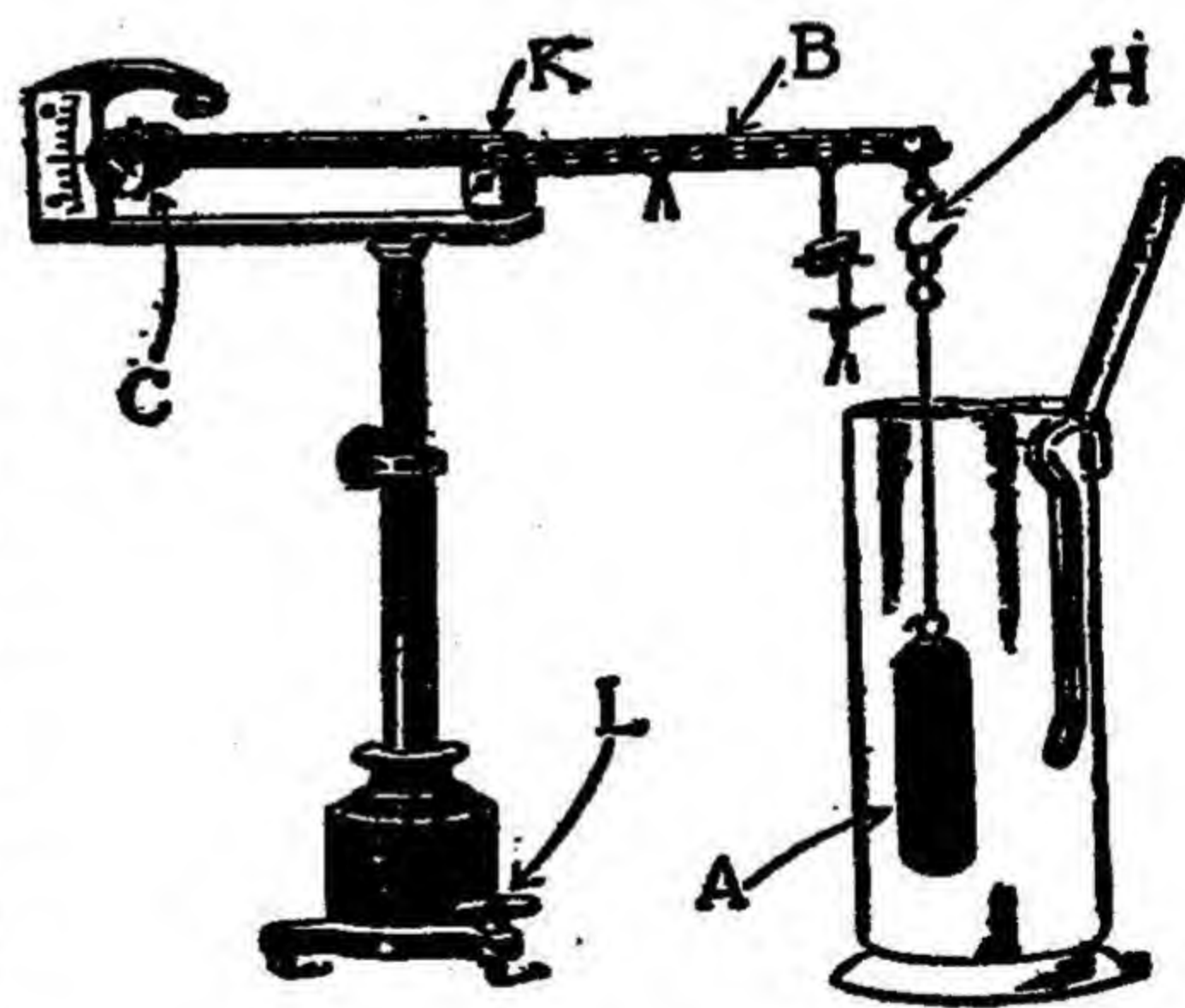


FIG. 21

The bob A has a definite volume, e.g. 10 cc., and when it is completely immersed in a liquid it is therefore buoyed up by an amount equal to the weight of the 10 cc. of liquid displaced. If this weight were then hung on the hook H, while the bob is immersed in the liquid, the beam would be brought back to the original condition of balance. In the case of water at 25° C., 10



cc. weigh 9.971 g. and a weight of this much, generally of horse-shoe shape, is provided to be hung on hook H to achieve balanced equilibrium. When liquids of density greater than 1 are involved, the horse-shoe weight is used; when less than 1 it is not needed. A set of smaller weights, 0.1, 0.01 and 0.001 of the magnitude of the large weight, may be hung on pegs or in notches spaced along the beam at distances equal to  $1/10$  the distance from the knife edge *K* to the knife edge at the right-hand end. Hence by placing these fractional weights along the beam until equilibrium is attained, the density of the liquid may be determined. The surface tension effect where the platinum wire pierces the liquid surface is negligibly small.

(3) The *pycnometer* is one of the most convenient instruments for obtaining high accuracy in determination of density. It may



FIG. 22

take the form of a *specific gravity* bottle, shown in Fig. 22. An accuracy to the 4th or 5th decimal place can be realized, depending on the size of the bottle, the bore of the capillary, and the temperature control. The bottle is filled with the liquid, and then the ground glass stopper is inserted, so that the capillary tube in the stopper is filled. The overflow of liquid which spills out, as the stopper is pressed into place, is carefully wiped off with a piece of absorbent cloth. The volume of the bottle is first determined by filling it with distilled water, from which the dissolved air has been removed by boiling, or in a vacuum desiccator, and then weighing. The liquid, the density of which is to be determined, is then introduced in the same manner into the clean, dry bottle, and weighed. The largest error is due to evaporation, both from the capillary, and particularly through the ground glass joint. Sometimes a ground glass cap is provided to cover the top of the bottle, its function being to cut down the evaporation, and also to catch any liquid which would otherwise spill out by expansion, in case the temperature of the balance case, where the weighing is made, is higher than the temperature at which the bottle is filled. Many modifications of the specific gravity bottle are in common use, one of which is provided with a thermometer inside the bottle. If the conditions of the determination justify it, the correction for buoyancy of air should be made (described below).



An excellent form of the pycnometer is the Ostwald type, shown in Fig. 23. This pycnometer is also filled first with water and then with the liquid whose density is being sought. With a pycnometer glass bulb as large as 100 cc., and with capillary arms of a little less than 1 mm. bore, and with careful weighing to 0.1 mg., it is possible to determine density with this instrument almost to 1 part in a million. The pycnometer should first be thoroughly cleaned, inside and out, rinsed repeatedly with distilled water, and dried thoroughly. Then it is immersed in the water of a thermostat bath (say at 25°) to wet it on the *outside*, and is rubbed dry for 1/2 minute with an absorbent cloth. This procedure is to reproduce the same sort of treatment of the glass before the empty pycnometer is weighed as must be carried out later with the filled pycnometer. Weigh. Then the pycnometer may be filled with liquid (water first) by attaching a flexible rubber tube on the right-hand arm and sucking liquid in through the tip of the opposite arm. The pycnometer is then immersed in a horizontal position into the thermostat water, with temperature control to 0.01°, up as far as marks A and B on the capillaries just above the platinum wire, by which the instrument is to be suspended (both in the thermostat and in the balance). Allow it to stand in thermostat for 30–40 minutes, and finally adjust the meniscus on the left and on the right so that they both stand exactly (within 0.1 mm.) at the two ring marks A and B which have been etched on the glass with hydrofluoric acid. (See Exp. 17.) If a little more liquid needs to be introduced, it may be sucked in through the tip. If some needs to be removed, a piece of filter paper or blotting paper should be touched to the tip near A, and at the same time one should blow gently at B through a flexible rubber tube to displace the liquid to the left until it contacts with the absorbent paper. This adjustment to the two marks A and B should be made with great care. Then remove, wipe with the cloth as before and weigh.

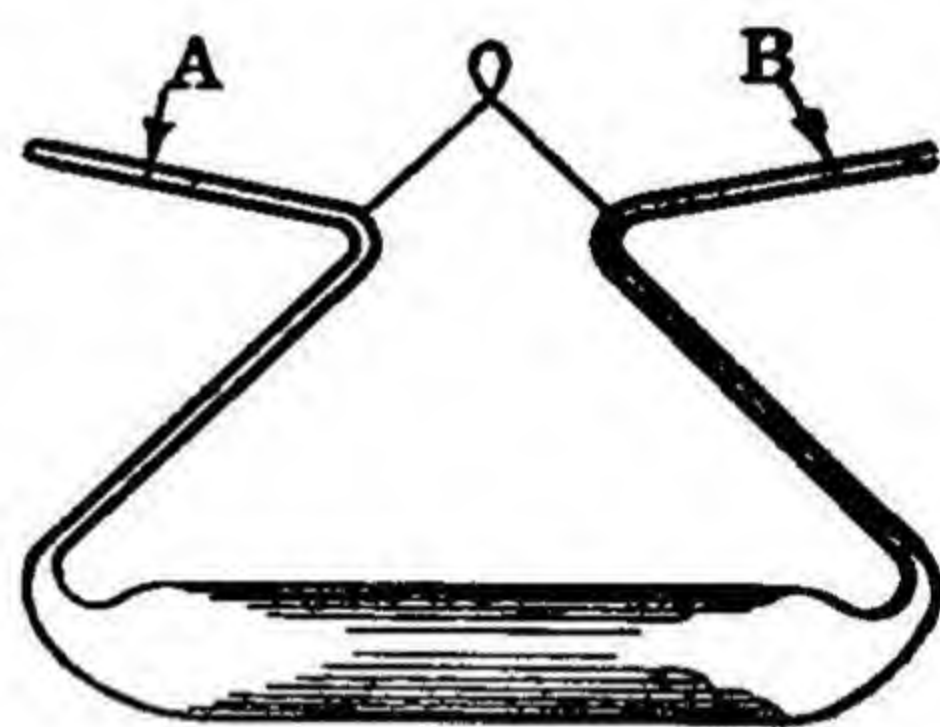


FIG. 23

The weight must be corrected for buoyancy of air. If 0.0012 g. is the weight of 1 cc. ordinary air at room temperature, and if we



have some body of density  $d$  counterpoised on a balance by brass weights  $G$ , the true weight of the body is

$$G + \frac{0.0012 G}{d} \text{ grams.}$$

But the true weight of the brass weights is not  $G$ , but  $\frac{0.0012 G}{8.5}$ , where 8.5 = density of brass. The true weight of the body is, therefore,

$$\begin{aligned} & G + \frac{0.0012 G}{d} - \frac{0.0012 G}{8.5} \\ &= G \left( 1 + \frac{0.0012}{d} - \frac{0.0012}{8.5} \right) \\ &= G \left( 1 + \frac{0.0012}{d} - 0.00014 \right). \end{aligned}$$

To get the weight of the substance in vacuum the quantity  $\left( \frac{0.0012}{d} - 0.00014 \right)$  g. must be added to each gram of apparent weight.

For convenience a table of the densities of pure water, g./cc., over a range of temperature from 0°–30° C., is included here.

TABLE VI  
DENSITIES OF WATER

Temp.	Density	Temp.	Density
0°	0.999874	21°	0.999023
4°	1.000000	22°	.997800
5°	.999992	23°	.997568
10°	.999731	24°	.997326
15°	.999132	25°	.997073
16°	.998976	26°	.996811
17°	.998808	27°	.996540
18°	.998628	28°	.996260
19°	.998437	29°	.995971
20°	.998235	30°	.995674

**Exercises for the Student.** (1) Because of the great widespread interest in "heavy water," the student may care to prepare some appreciably concentrated heavy water as follows. Make up 2000 cc. of 0.3–0.4 N aqueous NaOH solution. Place 400 cc. in



each of five 500 cc. glass bottles and pass a d.c. electric current, 5-7 amperes, through the solutions in series, using soft *iron* strip electrodes bent into an inverted U-form, thus  $\Omega$ , with one arm dipping into one bottle and the other into another one, etc. Keep the temperature down to 20°-25° by circulating tap water around the bottles. Electrolyze for about 5 days until the volume is reduced to 1/10 the original volume, meantime, however, combining the reduced volumes, and ending with all of the solution (200 cc.) in one bottle. Distill off the water, using preferably an iron or copper still (because of the solvent effect of the hot conc. alkaline solution on glass), and redistill from a fractionating glass flask *twice*, to be sure that all alkali, which may spatter over into the distillate to a slight extent, is eliminated. Measure the density with an Ostwald pycnometer of 50 to 100 cc. volume.

Most of the heavy hydrogen is left behind in the solution, in such an electrolysis, as heavy water molecules  ${}^2\text{H} - {}^{16}\text{O} - {}^2\text{H}$ , with a molecular weight of 20, as contrasted with light water molecules  ${}^1\text{H} - {}^{16}\text{O} - {}^1\text{H}$  of molecular weight 18. (We will not consider here the concentration of heavy oxygen.) A concentration of about 10 times the original concentration of heavy water molecules in normal water is yielded by reducing the volume of the NaOH solution to 1/10 by electrolysis. The difference is easily detected with an Ostwald pycnometer. See the following references on heavy water: Washburn and Urey, *Proc. Nat. Acad. Sci.*, 18, 496 (1932); Urey, Brickwedde and Murphy, *Phys. Rev.*, 39, 164 (1932); Lewis and Randall, *J. Chem. Phys.*, 1, 341 (1933); Taylor, Eyring and Frost, *J. Chem. Phys.*, 1, 823 (1933); Urey, *Science*, 78, 566 (1933).

(2) Aqueous cane sugar solutions in a series of step-wise concentrations may be made up, the densities determined, either at a single temperature or over a range of temperatures, either with a Mohr-Westphal balance, or with a specific gravity bottle, or with an Ostwald pycnometer, and the results compared with densities found in handbook tables. In order to familiarize himself with the various conventional methods for expressing concentrations, the student should select one or more of the solutions, and from the measured density and the known weights of sugar and water, calculate the concentration in the following terms: (a) grams of



solute per 100 grams of solvent, (b) mol fraction, (c) molality by weight, (d) molality by volume.

(3) **Preparation of Constant Boiling Hydrochloric Acid.** Starting with 800 cc. hydrochloric acid of density about 1.100, distill off about 600 cc. Then collect 150 cc. (noting barometer reading) and keep in sealed glass tubes. The following quotation is from Hulett and Bonner, *J. Am. Chem. Soc.*, 31, 390 (1909).

"By starting with hydrochloric acid,  $d = 1.10$ , made up with an ordinary hydrometer or a specific gravity balance, and distilling off  $3/4$  of the liquid taken, the following distillate should not differ by more than one part in 10,000 from the figures given in the following table. This constant boiling hydrochloric acid is not hygroscopic or noticeably volatile and may be easily weighed in a little flask. By using a capillary pipette joined to a piece of flexible rubber tubing, to adjust the last amount of acid, it is a very simple matter to weigh out 180.170 g. to less than 10 mg. and this will give a normal solution (when diluted to 1000 cc.) with an accuracy that is seldom attained even with elaborate precautions.

Pressure	Percent HCl	Grams const. boiling distillate for 1 mol HCl	Density 25°
770	20.218	180.390	1.09607
760	20.242	180.170	1.09620
750	20.266	179.960	1.09633
740	20.292	179.745	1.09646
730	20.314	179.530	1.09659

Both  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  give constant boiling mixtures but seem to be less desirable in several particulars than hydrochloric acid, which may serve as a reference basis, directly or indirectly, for most solutions" — in quantitative analytical work.

Measure the density of your sample of constant boiling hydrochloric acid with an Ostwald pycnometer, and compare with the results of the above table. The number of grams of constant boiling distillate for 1 mol of HCl given in the third column has, of course, been determined by quantitative analysis of the distillate for HCl.



## EXPERIMENT 10

### VISCOSITY OF LIQUIDS

In several current text-books of physical chemistry, the unit of viscosity is defined as the *force* necessary to cause two parallel liquid surfaces of unit area to slide past one another with unit velocity. Criticize this definition from the point of view of dimensional reasoning, and give a correct definition of a *poise*. The viscosity  $\eta$  of a liquid flowing through a capillary tube may be calculated by Poiseuille's equation.

$$\eta = k \cdot \frac{pr^4t}{Vl}$$

where  $k$  is a proportionality constant,  $p$  the hydrostatic pressure forcing the liquid along,  $r$  the radius of the capillary,  $t$  the time of delivery of the volume  $V$ , and  $l$  the length of the capillary tube.

The constant  $k$  is a number, having the value  $\frac{\pi}{8}$ . This equation can be derived both empirically and theoretically (see, e.g., Bingham, *Fluidity and Plasticity*, pp. 8-16, McGraw-Hill, 1922). A correction must be introduced into this equation because the liquid which leaves the capillary tube possesses kinetic energy. The corrected form of the equation is

$$\eta = \frac{\pi}{8} \frac{pr^4t}{Vl} - \frac{Vd}{8\pi lt} \times 1.12$$

where  $d$  is the density of the liquid. By choosing a long capillary of small bore,  $V$  will become small and  $t$  large, and this arrangement makes the correction term very small compared with the first term. In the present experiment this correction may be neglected. Show that the dimensions of the two terms on the right-hand side of the equation are the same.

#### (A) OSTWALD VISCOSIMETER

The Ostwald viscosimeter, shown in Fig. 24, is generally employed to determine the viscosity of liquids. The large bulb B is about two-thirds filled with a known volume of the liquid under



investigation. With a rubber tube attached at S, suction is applied and the liquid drawn up above the mark *a* at the top of the small bulb *b*. The liquid is then allowed to drain back through the capillary, and the time required for the meniscus to pass from the point *a* to the point *c* is measured with a stop-watch. If now this

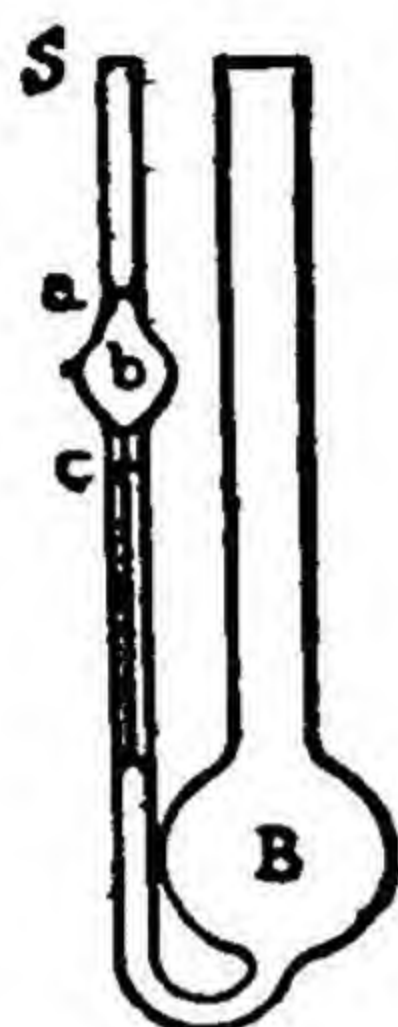


FIG. 24

liquid is replaced with an equal volume of another liquid, and the time required for the bulb *b* to empty is again obtained the viscosities  $\eta_1$  and  $\eta_2$  of the two liquids will be related as follows:

$$\frac{\eta_1}{\eta_2} = \frac{\pi}{8} \cdot \frac{p_1 r^4 t_1}{V l} \bigg/ \frac{\pi}{8} \cdot \frac{p_2 r^4 t_2}{V l} = \frac{p_1 t_1}{p_2 t_2}$$

since  $r$ ,  $V$  and  $l$  are the same in both cases. The two hydrostatic pressures  $p_1$  and  $p_2$  are in the same ratio as the two densities,  $d_1$  and  $d_2$  of the liquids, providing the hydrostatic heights are the same in the two cases, as of course they would be if  $V_1 = V_2$ .

Hence the relationship may be stated

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad (1)$$

#### EXPERIMENTAL

(a) Set up an Ostwald viscosimeter (which has been thoroughly cleaned with hot chromic acid solution) in a water thermostat with glass sides, so that the viscosimeter can be easily observed. The capillary tube should be chosen so that the time of delivery of 5–6 cc. water will be about 100 seconds. Determine the time of delivery of distilled water, freshly boiled to remove dissolved air, at 25.0°. The water must be allowed to stand in the viscosimeter about 10 minutes to attain the temperature of the thermostat. Obtain the average of four determinations. The absolute viscosity of water at 25° is 0.0088 poise. By using Equation 1, the viscosity of any other liquid relative to that of water, or its absolute viscosity, can be calculated if the density of the liquid and its time of delivery in the viscosimeter are known.

Determine the absolute viscosities of water at 30.0°, 35.0° and 40.0°, by adjusting the temperature of the thermostat, and assuming that the length and radius of the glass capillary are un-



affected by the rise in temperature, and looking up the density of water at the various temperatures in a reference table. In each case obtain the average of four determinations. Plot the absolute viscosities against temperature. What is the percentage decrease in the viscosity of water for a rise of  $1^{\circ}$  at the temperatures  $25^{\circ}$ ,  $30^{\circ}$ ,  $35^{\circ}$  and  $40^{\circ}$ ?

(b) Determine the absolute viscosities at  $25^{\circ}$  of a one mol-per cent solution of methyl alcohol in water, and the same of ethyl, *n*-propyl, *n*-butyl alcohols, and glycerine, glucose and sucrose. These stock solutions are made up so that the ratio of the mols of solute to mols of water is 1 : 99. In case of the last three solutions a small trace of mercuric iodide is added to prevent fermentation. Again obtain the average of four determinations in each case. Determine the densities with a Mohr-Westphal balance (see Exp. 9). Plot the absolute viscosities against the molecular weights of the solutes, against their molecular volumes, against the number of carbon atoms in the respective molecules, and against the total number of atoms in each molecule. Which one of these properties of the solute seems to be most important in fixing the viscosity of the solution?

From the measurements made above with the solutions of the alcohols it becomes apparent that the magnitude of viscosity depends to some extent on the general property of molecule size. But in general a far more important factor is the operation of cohesive forces between neighbor molecules, i.e. van der Waals' forces, which to a certain extent bind the neighbor molecules together, or at least reduce mobility and "stiffen up" the liquid. Some of the common atoms which enter into the structure of molecules possess much larger van der Waals' forces than others. For example, *oxygen atoms*, lying in the surfaces of molecules, give rise to very strong cohesive attractions for other atoms in the surfaces of neighbor molecules (compare with the discussion of polar oxygen-bearing groups in Exp. 12).

As an illustration of the effect of the presence of oxygen atoms on viscosity let us take the case of some ethane substitution products.  $C_2H_6$  itself is a gas at ordinary temperatures, i.e. its cohesive forces are relatively small. But in  $CH_3 \cdot CH_2 \cdot OH$ , containing 1 oxygen atom, the forces are large enough to bind the molecules together in the liquid form; and the viscosity of ethyl alcohol is of



course much greater than that of ethane. In  $\text{HO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , ethylene glycol, the viscosity becomes much greater than in  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{OH}$ . If still further oxygen atoms are substituted

into the molecule, as in oxalic acid,  $\text{HO}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{OH}$ , the van der Waals' forces per molecule become so great that the molecules are bound rigidly together in a crystal lattice, and we get a solid. The student should pursue this line of thought for himself, and correlate viscous properties with the oxygen atom population in various commonly known organic molecules; for example, develop the series of propane substitution products. An article by Dr. Langmuir, *Chem. Rev.*, 6, 451-79 (1929), is most interesting in this general connection.

### (B) THE FALLING BALL METHOD

(See Reilly, *Physico-Chemical Methods*, pp. 364-6; Gibson and Jacobs, *J. Chem. Soc.*, 117, 473 (1920))

According to Stokes' law the uniform velocity  $v$  of a sphere falling vertically through a liquid of viscosity  $\eta$  is

$$v = \frac{2gr^2(d_1 - d_2)}{9\eta}$$

where  $r$  is the radius of the sphere,  $d_1$  its density,  $d_2$  the density of the liquid, and  $g$  the acceleration of the earth's gravitational field.

Ladenburg (*Ann. Physik*, 23, 9, 447 (1907); 22, 287 (1907)) has mathematically derived corrections for the wall-effect, i.e., the influence of the wall of the tube on the velocity, and for the end-effect of the bottom of the tube, which must be applied to the simple Stokes' equation for the case of a small sphere falling axially through a viscous liquid in a cylindrical tube. The velocity corrected for the wall-effect is  $v(1 + 2.4r/\rho)$  where  $\rho$  is the radius of the cylinder. This is experimentally valid but fails when  $r/\rho$  is large. The velocity corrected for the end-effect, when measured in the middle third of the tube, is  $v(1 + 3.3r/h)$  where  $h$  is the height of the liquid.

The complete expression is therefore

$$v\left(1 + 2.4\frac{r}{\rho}\right)\left(1 + 3.3\frac{r}{h}\right) = \frac{2gr^2(d_1 - d_2)}{9\eta}$$



or if the time of fall  $t$  through a distance  $l$  is measured

$$\frac{l}{t} \left( 1 + 2.4 \frac{r}{\rho} \right) \left( 1 + 3.3 \frac{r}{h} \right) = \frac{2 gr^2 (d_1 - d_2)}{9 \eta}$$

If spheres of equal radius are used in tubes of the same dimensions in a series of determinations with different liquids or at different temperatures all of the above quantities are practically constant except the viscosity and density of the liquid and the time of fall. Then

$$\eta = K(d_1 - d_2)t$$

where

$$K = \frac{2 gr^2}{9 l(1 + 2.4 r/\rho)(1 + 3.3 r/h)}$$

is a numerical constant involving all the corrections for the particular tube used.  $K$  is called the tube constant.

If now one measures the time of fall through a liquid whose density and viscosity are known, the tube constant  $K$  can be evaluated and then the equation  $\eta = K(d_1 - d_2)t$  can be used to determine the viscosity of other liquids. In practice it is much more convenient to standardize the tube, i.e., determine the tube constant in this way, than to calculate the corrections to be applied. Furthermore, the influence of inaccurate measurements of the radii of the spheres and of the tube is totally eliminated, as is also the influence of slight variations in the dimensions of the tube.

#### APPARATUS

Figure 25 shows the apparatus. It consists of a glass container tube 30 cm. long with an internal diameter of 2 cm. Marks extending around the tube are etched at a distance of 6 cm. from the open end and then at successive intervals of 5 cm.

The top of the tube is closed with a one-hole rubber stopper through which passes a glass delivery tube of 2 or 3 mm. internal diameter and 9 or 10 cm. long. An improvement which keeps the delivery tube in the center may be improvised by using two one-hole rubber stoppers and a piece of glass tubing 5 cm. long which will just slide into the container tube, as indicated in the figure.

For the spheres, steel balls 1/16 of an inch in diameter (from



ball-bearings) are used. Balls  $1/8$  of an inch in diameter may be used but in this case the delivery tube ought to be of larger bore and, since the velocity of fall will be greater, the length of the tube may advantageously be increased, thus increasing the distance

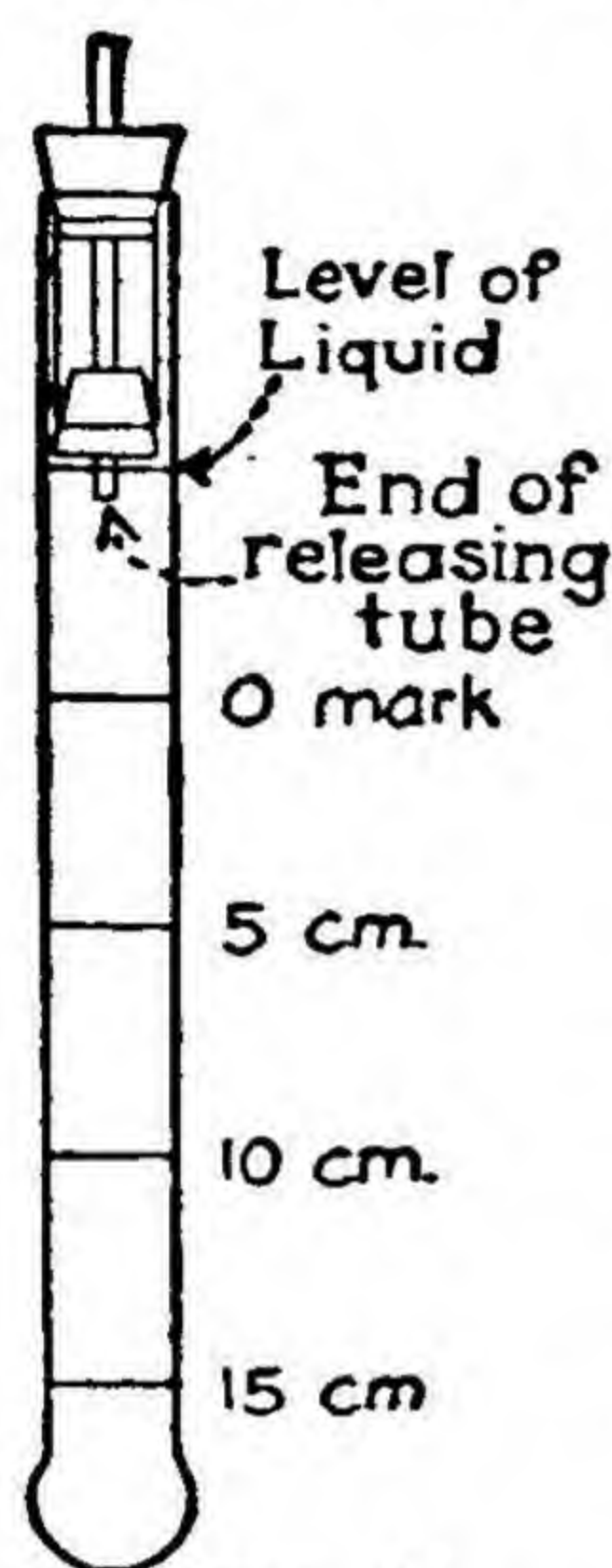


FIG. 25

through which the time of fall is measured. However, lengthening of the tube makes it more difficult to maintain the whole at a definite temperature. The balls should be of uniform size. Unless they are guaranteed by the makers to be of a certain size within rather narrow limits (say  $\pm 0.0004$  cm.) it is advisable to test their uniformity of size with a micrometer and to discard those that fall outside these limits.

The time of fall is measured with a stop-watch. This need not be a very accurate instrument as only the relative time of fall is needed. If a stop-watch with two hands be used it is possible to measure the time of fall through each 5 cm. interval of the 15 cm. distance and determine that the sphere is falling with uniform velocity.

A pycnometer or specific gravity bottle is necessary for determining the density of the liquids. (See Exp. 9.) A form of pycnometer especially suited for use with viscous liquids is that described by Johnston and Adams (*J. Am. Chem. Soc.*, **34**, 566 (1912)), a description of which is also given in Reilly, "*Physico-Chemical Methods*," p. 305. The essential point in this type of pycnometer is that the cover and the top of the neck are ground optically flat. The neck is made unusually heavy to make it rigid and to minimize conduction of heat from the fingers when handling. An accessory apparatus described by Newkirk (*Bureau of Standards, Technologic Papers*, 161 (1920)) is of great value in removing bubbles introduced with the liquid. This, together with the Johnston and Adams pycnometer, is illustrated in Fig. 26. It is attached to the pycnometer by a ground glass joint and a partial vacuum is created with a water pump. The stop-cock, which is

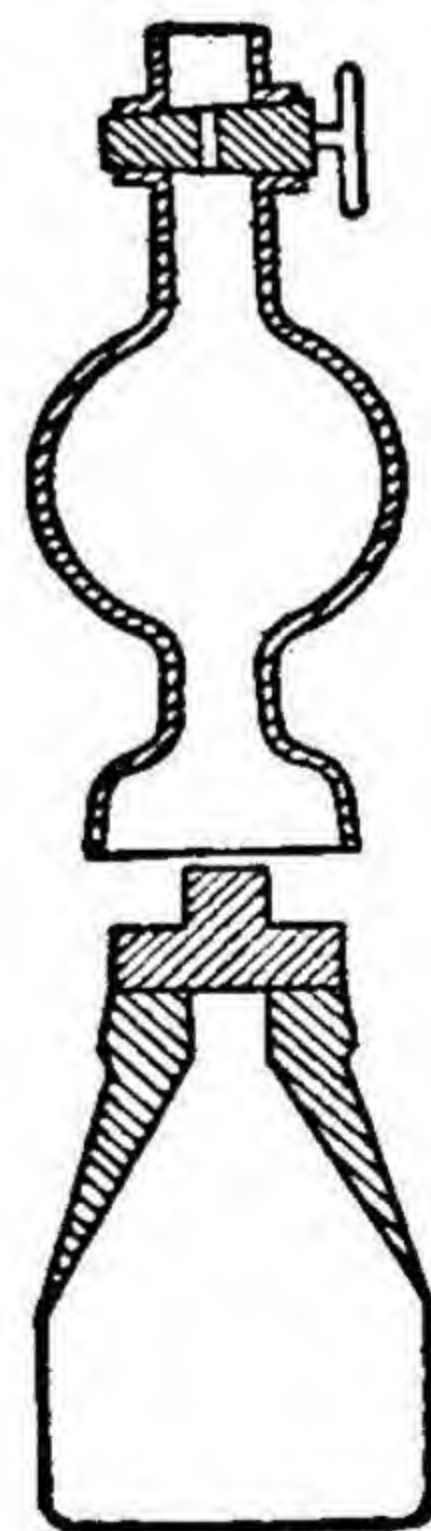


FIG. 26



lubricated with the liquid whose density is being determined, is then closed, and the whole is allowed to stand until the bubbles have come to the surface.

#### MANIPULATION

To standardize the fall tube it is filled to the upper mark with castor oil, whose density and viscosity at the temperature used are known. The delivery tube is inserted and adjusted so that it is coaxial with the large tube and its end dips from 0.5 to 1 cm. below the surface of the liquid. The whole is now placed in a thermostat maintained at the desired temperature to  $0.1^{\circ}\text{C}$ . The thermostat must have at least one transparent side. If no such thermostat with a motor driven stirrer is at hand a one-liter graduate cylinder or similar long glass vessel provided with a wire stirrer may be used.

After the castor oil has reached the temperature of the thermostat, which requires 15 or 20 minutes, a ball is dropped down the delivery tube. As it slowly travels down this tube it becomes freed from air bubbles and leaves the end in the center of the tube and with the minimum of disturbance. It is allowed to travel through the first division and then its time of fall through the next 15 cm. is measured with a stop-watch.

Care must be taken that the delivery tube is coaxial with the large tube and that the latter is vertically placed. A length of thread with a small weight attached at one end may be held between the edge of the tube and the eye to facilitate making the proper alignment; this alignment should of course be made in two directions at right angles to each other.

The above procedure is repeated several times and the mean time of fall is found. It is important that the temperature be maintained constant as a slight change in temperature materially changes the viscosity and therefore the time of fall.

The density of the balls must be accurately determined, as the density of steel varies considerably. This may be done by measuring the diameter of a large number of the balls with a good micrometer, assuming spherical shape and calculating the volume; or by the displacement of a liquid in a pycnometer. If only a small number of balls (less than fifty) is available the former method is more accurate than the latter. In the displacement



method, if  $a$  be the weight of the balls,  $b$  the weight of the vessel filled with the standard liquid the density of which is  $d$ , and if  $c$  be the weight of the vessel filled with liquid and containing the weight  $a$  of the balls, then the density of the balls is  $ad/(b - c + a)$ . In this method it has been found that a diminutive pycnometer of the Ostwald type, of about 1 or 2 cc. capacity, with one of the arms of sufficient internal diameter to permit the entrance of the spheres, is a very satisfactory type. It can readily be made from a piece of glass tubing and should be used with another pycnometer of similar form and size as a tare. Pycnometers having ground glass joints are particularly troublesome because of evaporation of the liquid at the joints. (See Exp. 9.)

Using the data determined with the liquid of known viscosity, the tube constant  $K$  is calculated. The tubes and balls are thoroughly cleaned and the procedure is repeated with another liquid. Using the tube constant just found the viscosity of this liquid is then calculated.

#### EXPERIMENTAL

Determine the tube constant with castor oil at 20° C., using the values for the density and viscosity given in the table below, and then determine the viscosity of castor oil at 5.0°, 10.0°, 15.0°, 25.0° and 30° C. Repeat with another liquid such as recently boiled glycerine or the commercial product known as Karo syrup. In each case plot the viscosity against the temperature, and predict the viscosity at 30° before making the determination at 30°.

The following values for the density and viscosity of castor oil are taken from the table compiled from the data of Kahlbaum and

TABLE VII

Temperature (°C.)	Density (g./cc.)	Viscosity (poises)
5	0.9707	37.60
10	0.9672	24.18
15	0.9638	15.14
20	0.9603	9.86
25	0.9569	6.51
30	0.9534	4.51
35	0.9499	3.16
40	0.9464	2.31



Raber, published by the *Bureau of Standards (Technologic Papers, 24 (1918))*.

For the density of glycerine make use of the formula of Kailan (*Z. anal. Chemie, 51, 84 (1912)*)

$$d_4^t = 1.26413 + (15 - t)0.000632$$

where  $t$  is the temperature on the Centigrade scale.

REFERENCES:

- Taylor, Chap. IV.
- Rodebush, Chap. III.
- Getman and Daniels, Chap. III.
- Millard, Chap. III.
- Findlay, Chap. IV.
- Bingham, *Fluidity and Plasticity*.
- Hatschek, *The Viscosity of Liquids*, G. Bell & Sons.



## EXPERIMENT 11

### SURFACE TENSION

#### (A) DU NOÜY TENSIMETER; (B) DROP WEIGHT METHOD

If a film of liquid were suspended on such a frame as that shown in Fig. 27, so that the film could be stretched by pulling on P, it would be found that a "pull" force would have to be exerted at P to prevent the film from shrinking. This tendency of the film to contract is a manifestation of its surface tension. The force

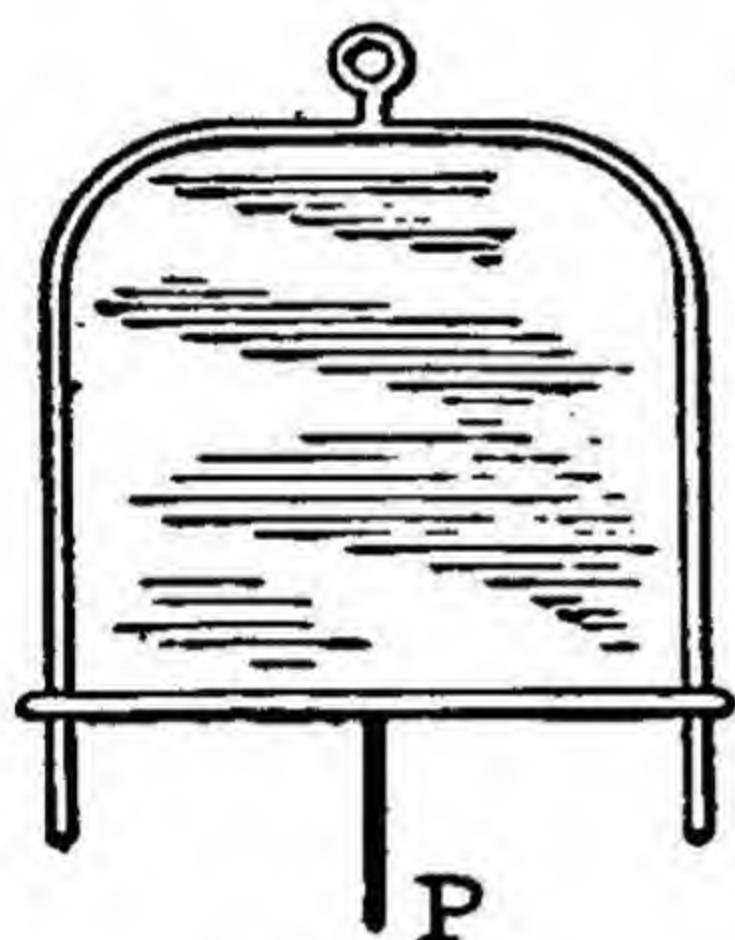


FIG. 27

required to prevent contraction is naturally greater, the wider the film, but it is independent of the length of the film. (See Willows and Hatschek, *Surface Tension and Surface Energy*, Chap. I, Blakiston.) That force which is just barely large enough to cause infinitely slow stretching of a film one centimeter wide, or which will just prevent shrinkage of a film of this width, is known as the surface tension. Surface tension is measured in dynes/cm. The student should state the dimensions in terms of L, M and T. Has the unit of sur-

face tension been given a special name of its own?

The frame in Fig. 27 really supports two film surfaces, front and back, and the surface tension for a single surface is therefore obtained by dividing the force exerted per unit width by 2. The measurement illustrated in this figure has been highly idealized, for as a matter of fact very few solutions form double surface films of this sort which are stable for a sufficient length of time to permit the measurement of their surface tension, and *no pure liquids* seem to persist as thin films for more than a fraction of a second. The results to be expected from a measurement of this sort may, however, be achieved by other methods, as for example, by the method of the du Noüy tensimeter, presently to be described.

Several methods for measuring surface tension have been de-



veloped, among which may be mentioned: (1) the capillary tube, (2) the falling drop (the stalagmometer), (3) the air bubble method, (4) the surface ripple method, and others. (1) and (2) particularly have been developed to a state of considerable precision, and have been generally used in many investigations involving systematic surface tension measurements. Directions for both the tensimeter method and method (2), with falling drops, will be given here. For (1) the student is referred to Reilly, *Physico-Chemical Methods*, Chap. XXVII; Findlay, *Practical Physical Chemistry*, p. 74; and Richards and his students, *J. Am. Chem. Soc.*, 37, 1656 (1915); 46, 1196 (1924).

(A) The du Noüy Tensimeter. This instrument, designed by P. L. du Noüy (*J. Gen. Physiology*, 1, 521, 1919), is shown in Fig. 28. It consists of a fine steel wire, one end of which is securely held at the support F, and the other end is fastened to a worm-wheel controlled by the thumb-screw B. The worm-wheel also carries a pointer A which moves over a dial (graduated in degrees) when the wire is twisted by turning the thumb-screw. To the middle of the wire is clamped a light lever D on the end of which is suspended a stirrup carrying a platinum wire loop of just 4 cm. peripheral length (or of any convenient *known* length). To bring the instrument to the starting position, the pointer A is set at zero and then the torsion of the steel wire is modified by means of the adjusting screw F and the set screw O until the lever just fails to touch the platform E, the distance between them being about the thickness of a thin piece of paper. The liquid, the surface tension of which is to be measured, is contained in a watch-glass or small dish, supported on platform G. This is moved slowly upward with the screw provided for this purpose until the surface of the liquid touches the ring L. It is important that the ring be in good contact with the liquid. By turning the thumb-screw B the torsion of the wire is gradually increased until finally the platinum ring is torn suddenly away from the liquid. The angle through which

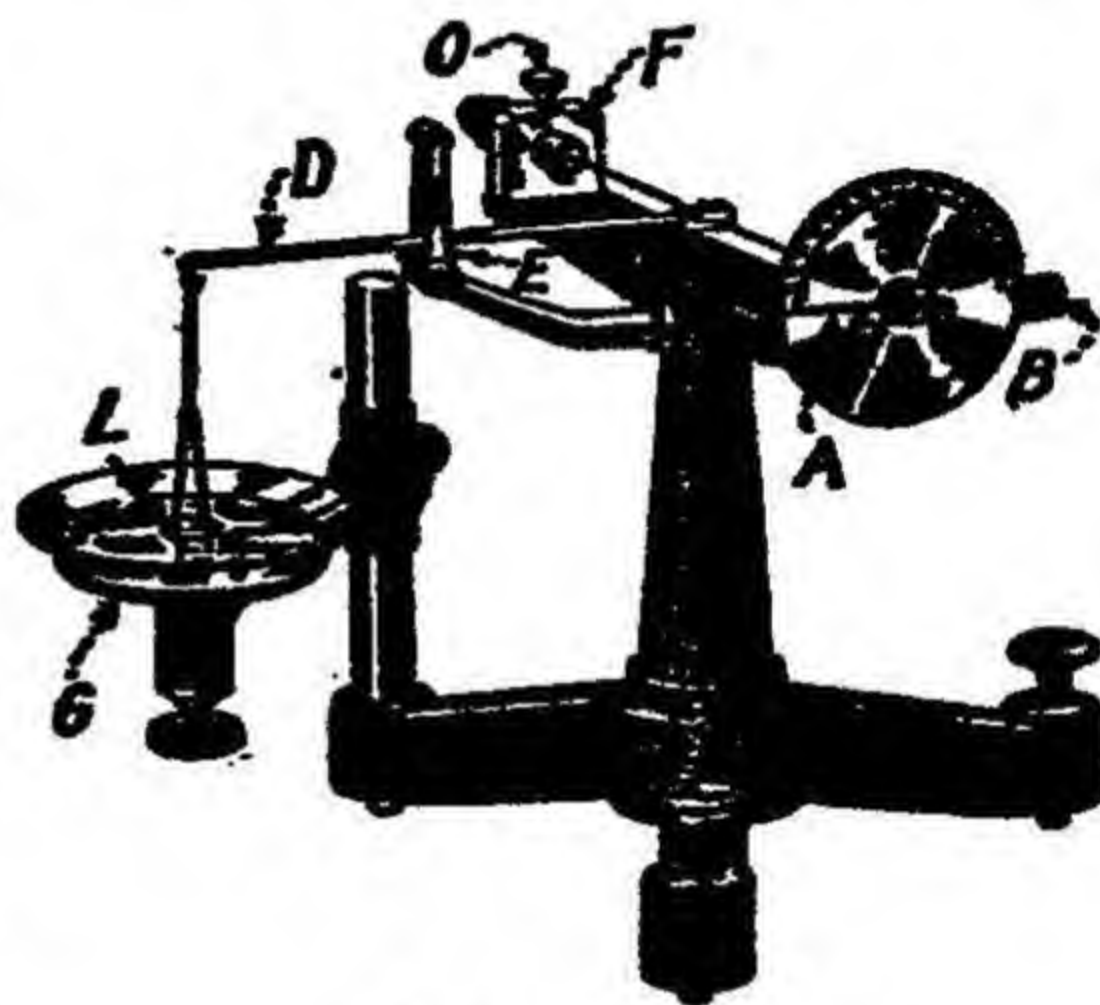


FIG. 28



the pointer has been turned is then read from the dial scale. In order to convert this angular reading directly to dynes/cm. of surface tension, the instrument must be standardized.

The standardization may be accomplished in two ways. In the first place, some liquid, such as water, of known surface tension may be employed, and the dial reading corresponding to this surface tension noted. This one calibration suffices for the whole scale, since the dial reading is proportional to surface tension. It is much more desirable, however, for the student to use the second method of standardization, which is independent of previously known surface tensions, and which makes the measurements, obtained with the instrument thus standardized, absolute and not relative. The method simply consists in adding to the platinum ring, when a certain torsion has been applied to the steel wire, enough weight to bring the lever D back to the starting position above platform E. It is satisfactory to add the weight by laying a short length of wire across the ring (No. 20, B. & S. gage copper wire is excellent) and subsequently weighing the wire on a balance. A somewhat more convenient procedure, amounting to the same thing as the above, is to bring the lever to the starting position with a dial pointer A at zero, and then to add the weight to the platinum ring and apply torsion until the lever is just barely lifted clear of platform E. The student should determine in this way the weights which just balance several degrees of torsion along the dial, for example,  $30^\circ$ ,  $60^\circ$  and  $90^\circ$ . If the dial can be read to  $1/10^\circ$ , how accurately should the weights of the several pieces of wire be determined?

The weights (expressed as grams) determined in this way may be converted to units of surface tension by first multiplying them by 980 to give dynes, then dividing by 4 cm. (the peripheral length of the ring) to give dynes/cm., and finally dividing by 2, since two liquid surface films are stretched as the ring is lifted off the surface.

The student's attention is called to the necessity of keeping the watch glass or other vessel containing the liquid *scrupulously clean*. It is well to wash such vessels with strong hot cleaning solution and with distilled water and to dry with a piece of clean cheese-cloth. The platinum ring should be held for a few seconds in a Bunsen burner flame (blue flame) until the wire glows. The ring



and inside of the watch glass should on no account be touched with the fingers.

The surface tension of water at room temperature as measured with the du Noüy tensimeter is about 3 dynes higher than the average value by other methods. The following explanation of this error is quoted from Klopsteg, *Science*, 60, 319 (1924).

“As the ring is drawn out of the liquid the upward force on the ring, measured by the torsion of the wire, is just balanced by the weight of liquid elevated above the normal surface. It is important to note that the scale readings of the instrument are taken with reference to the scale zero, and that the scale zero corresponds with the actual zero of torsion only when the arm which carries the ring is in its position of zero-balance. As the ring is pulled higher with increasing force, the true zero on the scale, with reference to which readings should be taken, shifts upward from the scale zero by an amount which corresponds to the position of the arm. Consequently, at the instant the film ruptures, the scale reading will be too high.”

A new technique has been developed for avoiding this error. For details the student is referred to the paper just quoted.

### EXPERIMENTAL

(1) **Surface Tension and Temperature.** With the du Noüy tensimeter standardized as directed above, determine the surface tension of distilled water at *room temperature*. Cool the water to a temperature near 0° C. and again measure its surface tension. In cooling the water, do not add ice directly to it, since ice usually is not free from impurities. Measure the surface tension of water at a temperature of 40°–50° C. A mercury thermometer of small bulb should be placed in the dish of water and near the platinum ring so that the temperature may be noted at the instant the ring escapes from the surface. The temperature can generally be controlled within 1°.

Plot the results, surface tension along the ordinate axis, temperature along the abscissa axis. Extrapolate to the temperature axis. Theoretically, this line should cut the temperature axis at the critical temperature,  $T_c$ . Actually it is aimed at a point 6° below  $T_c$ , but just before it reaches the axis it curls off and does



meet the axis at  $T_c$ . This statement seems to be true for all liquids.

Substitute your surface tension values at the three different temperatures in the Eötvös-Ramsay-Shields equation.

$$\gamma \left( \frac{M}{d} \right)^{\frac{2}{3}} = k(T_c - T - 6^\circ) \quad (1)$$

where  $\gamma$  = surface tension in dynes,  $M$  = molecular weight of water in the gaseous state,  $d$  = the density of liquid water,  $k$  = a proportionality constant,  $T_c$  = the critical temperature of water, and  $T$  = the temperature at which the surface tension  $\gamma$  is measured. Do your calculations show  $k$  to be really a constant? Show that  $k$  has the dimensions of energy divided by temperature; i.e., the same dimensions as  $R$ , the gas constant. For normal, non-associated liquids  $k$  generally has a value of about 2.12 ergs per degree. Ramsay and Shields have suggested that the degree of association of the molecules of a liquid may be calculated from the equation

$$x^{\frac{2}{3}} = \frac{2.12}{k} \quad (1A)$$

where  $x$  = the degree of association (or association factor) and  $k$  is the constant for the associated liquid, as for example, water. From your average value of  $k$  for water in the temperature interval  $0^\circ$ – $50^\circ$ , calculate  $x$ . Calculate the corresponding average molecular weight of liquid water. This last relationship is, however, extremely rough, and is not to be generally relied upon.

**(2) Surface Tension of Various Liquids.** Determine the surface tension at room temperature of benzene, ethyl alcohol, methyl alcohol, glycerine and aniline. Basing your opinion on the viscosity measurements made in Exp. 10, would you say that there is in general a simple relationship between the viscosity and surface tension of a liquid?

**(3) Surface Tension of a Solution.** Using a stock solution of 0.5 molar butyric acid (in distilled water), and suitable measuring pipettes for dilution, determine the surface tension at room temperature of 0.5, 0.4, 0.3, 0.2 and 0.1 molar solutions. Place the same quantity of each solution (say 5 cc.) on the watch glass, and in each case take the average of four surface tension determinations. Plot surface tension against concentration. During what



portion of the concentration range is the surface tension diminished to the greatest extent? Freundlich (*Colloid and Capillary Chemistry*, p. 66, Dutton; Kruyt and van Klooster, *Colloids*, Chap. II, Wiley; Ware, *Chemistry of the Colloidal State*, Chap. III, Wiley) has shown that the lowering of surface tension in solutions of moderate concentration may be represented by the equation,

$$\Delta\gamma = sc^{\frac{1}{n}} \quad (2)$$

where  $\Delta\gamma$  is the difference between the surface tension of the solution and that of the pure solvent,  $c$  is the concentration, and  $s$  and  $n$  are constants. Using logarithms of both sides we obtain

$$\log \Delta\gamma = \log s + \frac{1}{n} \log c. \quad (3)$$

Let the student test the validity of this equation for the butyric acid solutions by plotting the logarithms of  $\Delta\gamma$  against logarithms of the concentrations. By extrapolation estimate the surface tension of a 1.0 molar solution of butyric acid. Also plot  $\Delta\gamma$  against  $c$  on ordinary rectangular coordinate paper and on double logarithmic paper. Find the value of the constants  $s$  and  $n$  for butyric acid solutions.

In connection with the surface tension lowering of such solutions as that of butyric acid, what is Traube's rule?

(4) **Surface Tension of a Colloidal System.** Dilute a small portion of a stock aqueous solution of 0.0005 molar sodium oleate to 0.00002 molar and determine its surface tension at room temperature. Note the surface tension readings every minute for 15–20 minutes, and plot the readings against time. Interpret the results.

As a result of your experience with the du Noüy tensimeter, what would you say is the most serious objection to its use as a general means for the determination of surface tension? What are its outstanding advantages?

(B) **Weight of Falling Drop.** The surface tension of a liquid, as previously indicated, is the force tending to contract the surface, acting per unit length of line. The weight of a drop, as it is about to fall by detaching itself from a tip (may be made of glass), is balanced by the upward pull of the surface tension around the circumference of the drop. The weight of the drop which falls is



iven by Tate's law

$$W = m \cdot g = 2 \pi r \gamma \quad (4)$$

where  $W$  is weight,  $m$  mass,  $g$  acceleration of gravity,  $r$  radius of tip and  $\gamma$  surface tension. This relationship, however, is not quite exact. The weight  $W$  (or  $m \cdot g$ ) of the drop which falls also depends on the *shape* of the drop. It can be shown that  $W$  is some function  $f'$  of the ratio of the radius of the tip to the linear dimensions,  $l$ , of the drop. If  $V$  represents the volume of the drop we may substitute  $V^{\frac{1}{3}}$  for  $l$ .

$$f' \left( \frac{r}{l} \right) = f \left( \frac{r}{V^{\frac{1}{3}}} \right).$$

Hence, instead of Equation 4 we get the corrected equation

$$W = m \cdot g = 2 \pi r \gamma \cdot f \left( \frac{r}{V^{\frac{1}{3}}} \right). \quad (5)$$

Harkins and Brown, *J. Am. Chem. Soc.*, **41**, 519 (1919), gives a table of experimentally determined values for the correction factor  $f \left( \frac{r}{V^{\frac{1}{3}}} \right)$ .

TABLE VIII  
DROP-WEIGHT SURFACE TENSION CORRECTIONS

$\frac{r}{V^{\frac{1}{3}}}$	$f \left( \frac{r}{V^{\frac{1}{3}}} \right)$	$\frac{r}{V^{\frac{1}{3}}}$	$f \left( \frac{r}{V^{\frac{1}{3}}} \right)$
0.000	1.000	0.75	.6032
.30	.7256	.80	.6000
.35	.7011	.85	.5992
.40	.6828	.90	.5998
.45	.6669	.95	.6034
.50	.6515	1.00	.6098
.55	.6362	1.05	.6179
.60	.6250	1.10	.6280
.65	.6171	1.15	.6407
.70	.6093	1.20	.6535

For single liquids it is usually best to use such tips that  $\frac{r}{V^{\frac{1}{3}}}$  lies between 0.76 and 0.95.

**Directions.** The apparatus is shown in Fig. 29. The tip  $T$  of the capillary  $C$  should be made *flat*, and perpendicular to the axis



of the capillary, and with a perimeter edge around the lower end of the capillary as free as possible of imperfections, by rubbing with fine emery powder and water on a piece of plate glass lying horizontally on a table; or better, the grinding may be done in a lathe.

Clean the apparatus by pouring hot chromic-sulfuric acid cleaning solution through it. Without removing the capillary from the rubber stopper R above the tip, hold the tip just under the surface of hot cleaning solution for several minutes. Then rinse several times with distilled water. Be very careful not to allow grease from the hands to get on the tip, as the slightest trace of grease greatly lowers the surface tension of water. Fill the apparatus with distilled water and adjust the screw clamp so that the drops fall from the tip at a rate not greater than one a minute. Make sure that the liquid wets the tip clear out to the edge. Then, leaving unchanged the adjustment of the screw clamp, close the stop-cock so as to shut off the flow of water. Introduce one or two drops of water into the weighing bottle, B, stopper it with a carefully cleaned rubber stopper, and weigh carefully. Put the apparatus together and *immerse it completely* up to level LL in a large beaker of water at 20°. The vent tube V allows air to escape when the stopper R is inserted. The apparatus should be set on a firm base. Since the desks vibrate considerably, use the window ledges. As soon as the apparatus has come to the temperature of the water-bath, open the stop-cock and allow 10 drops of water to drop into the weighing bottle. Close the stop-cock, remove the weighing bottle, stopper, and weigh. Repeat with 10 more drops. If the two results do not check, continue until satisfactory checks are obtained. Determine in the same way the drop-weight of pure benzene at 20° C.

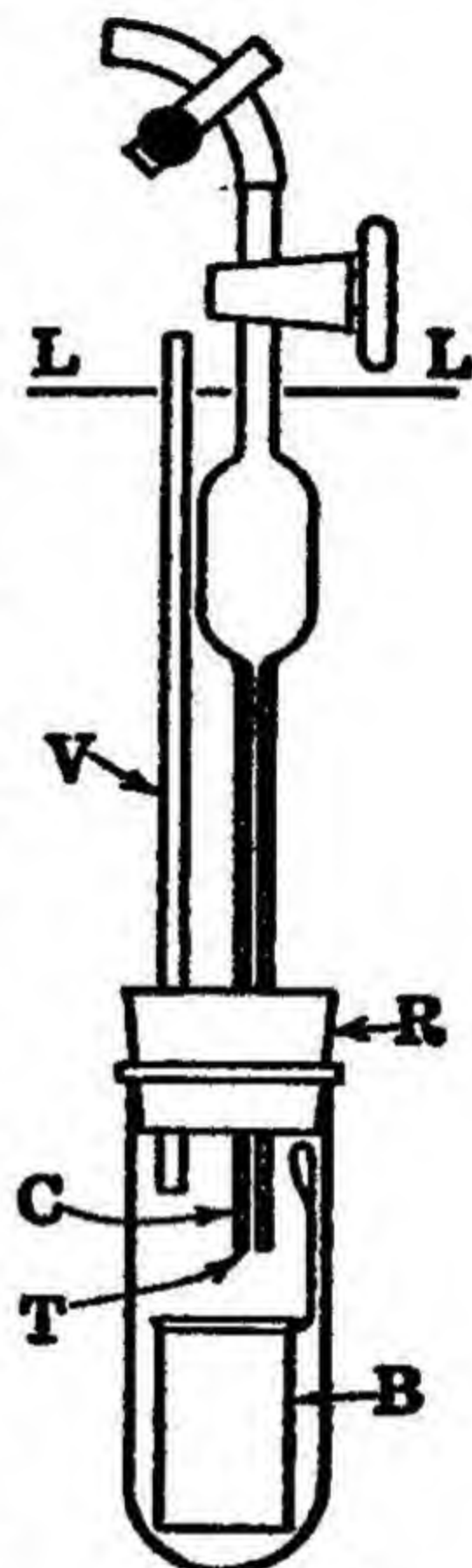


FIG. 29

**Calculations.** A graph of values of  $\left(\frac{r}{V^{\frac{1}{3}}}\right)$  against  $f\left(\frac{r}{V^{\frac{1}{3}}}\right)$  would be of assistance in interpolating to find the exact value of  $f\left(\frac{r}{V^{\frac{1}{3}}}\right)$  corresponding to the experimental value of  $\left(\frac{r}{V^{\frac{1}{3}}}\right)$  in each



of your determinations. Calculate the surface tensions from the drop-weights using Equation 5, above. Calculate the Eötvös-Ramsay-Shields constants from Equation 1(A).

The density of water may be obtained from Exp. 9, and the density of benzene may either be determined by one of the methods described in Exp. 9, or may be found in handbooks of physical constants.

**REFERENCES:**

- Taylor, Chaps. IV and XV.
- Rodebush, Chap. III.
- Getman and Daniels, Chaps. III and X.
- Millard, Chaps. III and XVI.
- Findlay, Chaps. IV and XX.



## EXPERIMENT 12

### OIL FILMS; MOLECULE SIZE AND SHAPE

In Exp. 10, in connection with viscosity, attention has already been called to the relatively large van der Waals' forces of oxygen, whenever it is to be found as one of the constituent atoms in a molecule. One of the interesting manifestations of its strong force field is the solubility of oxygen and oxygen-bearing groups in water. For example, ethane,  $C_2H_6$ , is quite insoluble in water, but the introduction of an oxygen atom to form ethyl alcohol,  $CH_3 \cdot CH_2OH$ , makes the molecule extremely soluble in water, as everybody knows. The  $CH_3 \cdot CH_2$  group may be thought of as still being insoluble, but as being drawn under and into the water by the strong tendency of the OH group to dissolve. If enough  $CH_2$  links are added to the chain molecule, however,  $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$ , the molecule becomes more and more insoluble as the proportion of the hydrocarbon part increases, until finally the solubility is very slight indeed, although the OH group on the end may still be soluble itself. Groups such as  $HSO_3$ ,  $COOH$ ,  $NH_2$ , and many other "polar" groups behave like OH. A simple experiment will now serve to illustrate the solubility of  $COOH$  groups, and also introduce the student directly to the subject matter of the present chapter.

**Experiment.** Clean two glass crystallizing dishes, 12-15 cm. diameter or larger, very thoroughly, first with soap, then chromic acid solution, and finally with distilled water. Fill each dish 1-3 cm. deep with distilled water. Pick out, with clean forceps, two small pieces of camphor and introduce a piece on each surface of water. Remembering that organic solutes generally lower the surface tension of water, can you account for the dancing motion of the camphor particles? Now dust a little talcum powder, or better, lycopodium powder (conveniently kept in a French square bottle with a few pieces of cheese cloth fastened over the neck with a rubber band) on to the two water surfaces. Then, on one surface



pour about 1/2 to 1 cc. of paraffin oil (or Nujol), *taken freshly* from a stock bottle. Notice that a lens-shaped pool of oil forms on the water surface, flattened out to some extent by gravity, and much thicker at the center than at the edges, but showing very little tendency (if the oil has not been contaminated by grease from the fingers) to *spread*. Then introduce on to the powdered surface in the other dish, one drop of oleic acid, using a medicine dropper. Notice that the oil instantly spreads almost to the confining walls of the dish, pushing the powder ahead of it. (The powder is added to the surface merely to improve the visibility.) Notice also that the camphor is still moving in the first dish, but stops its motion in the second dish as soon as the oleic acid has spread. Why? Now, further, with the medicine dropper carefully introduce 2 or 3 drops of oleic acid into the middle of the paraffin oil lens, and after about half a minute, when the oleic acid has diffused through to the bottom of the lens, notice the sudden explosive spreading. Other animal or vegetable oils, such as olive oil, cod-liver oil, peanut, corn, whale, cotton, lard oil, etc., may be substituted for the oleic acid. Many of us, as children, have played with the same spreading effect by cutting out little card-board fish or boats, with a channel cut from the stern end to a large hole near the middle, into which a few drops of olive oil were poured.

The point of this experiment, of course, is that oils like the mineral oils, made up of large purely hydrocarbon molecules,

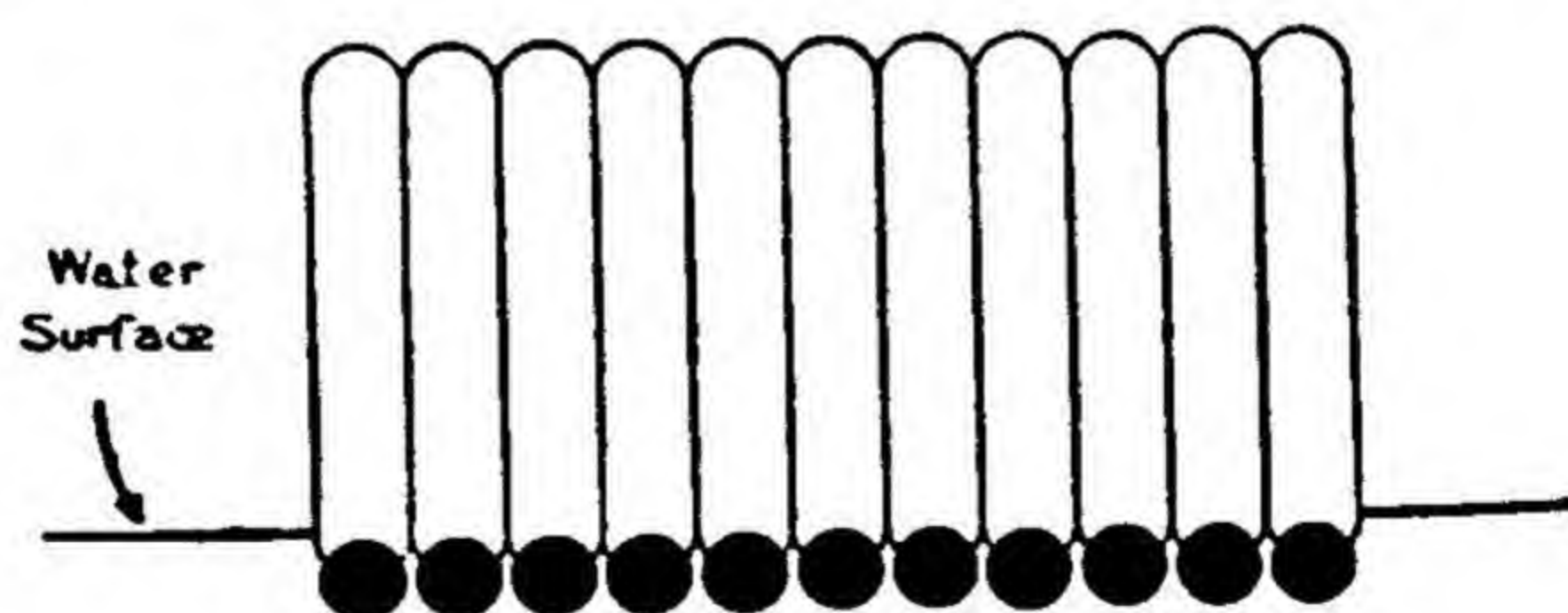


FIG. 30

not soluble in water, form oil bodies, on the water surface, with their molecules piled together as in the normal liquid state. But the molecules containing COOH groups or other polar groups at one end, spread out so that every soluble group can dissolve and stick under water, thus forming a thin film one molecule deep, with



the molecules oriented in a regular marshalled array, the soluble heads under water, and the long hydrocarbon tails sticking up vertically, as shown in Fig. 30.

Many investigators have played with oil films and speculated on the mechanism of spreading. Among these may be mentioned Lord Rayleigh, Fraülein Pockels, Hardy and Marcellin. Langmuir particularly and also Harkins, and more recently Adam and others, have developed an experimental technique for studying oil films quantitatively, and we shall now describe the construction and use of an apparatus for making such a quantitative study of oil films on a water surface. This apparatus can be constructed from easily obtainable materials if a few tools such as a soldering iron, a hacksaw, drills, etc., are available. The exact dimensions suggested in the following description are not essential.

#### CONSTRUCTION OF OIL FILM APPARATUS

The fundamental idea of the whole manipulation is to introduce a small known quantity of a spreading oil on to a water surface in a rectangular trough, and then to compress the oil film by moving a glass barrier, so that the trapped film is squeezed against a floating piston. The pressure on the piston is measured with a torsion wire arrangement and a circular protractor, very much as in the case of the du Noüy tensimeter, Exp. 11(A). The areas of a film squeezed together with different forces may then be studied, and the film areas of various oils at the same pressure may be compared.

A diagram of the apparatus is given in Fig. 31. The trough T is made of brass stock; the sides of  $3/8'' \times 3/4''$  stock, the bottom of  $1/4''$  plate brass. The inside dimensions are  $14.00 \times 60 \times 1.8$  cm. It is necessary that the inside width be constant and that the thickness of the edges be about 1 cm.; the rest of the dimensions are optional.

The balance frame K may be made of solid brass or of  $5/16''$  brass tubing. In the latter case brass bearings are soldered between two upright tubes comprising the frame. The frame is soldered to  $1/8''$  brass plates P which are held to the trough when in use by means of the clamps Q. The frame fits closely against the sides of the trough.

The bearings in the frame are 7.0 cm. from the base; they fit



closely the  $\frac{3}{16}$ " brass rods D and D', the axles of the torsion balance. The axle D' is threaded on the outside end and fitted with an adjusting nut B. A set screw A' in the bearing prevents it from turning after the adjustment is complete. The torsion wire E is made of phosphor bronze about 0.008" diameter, spring temper. (Note — may be obtained from Baker and Co., Newark, N. J.) It is soldered into the ends of D and D' as shown in the inset figure. A small hole,  $\frac{1}{32}$ " or less, is drilled longitudinally

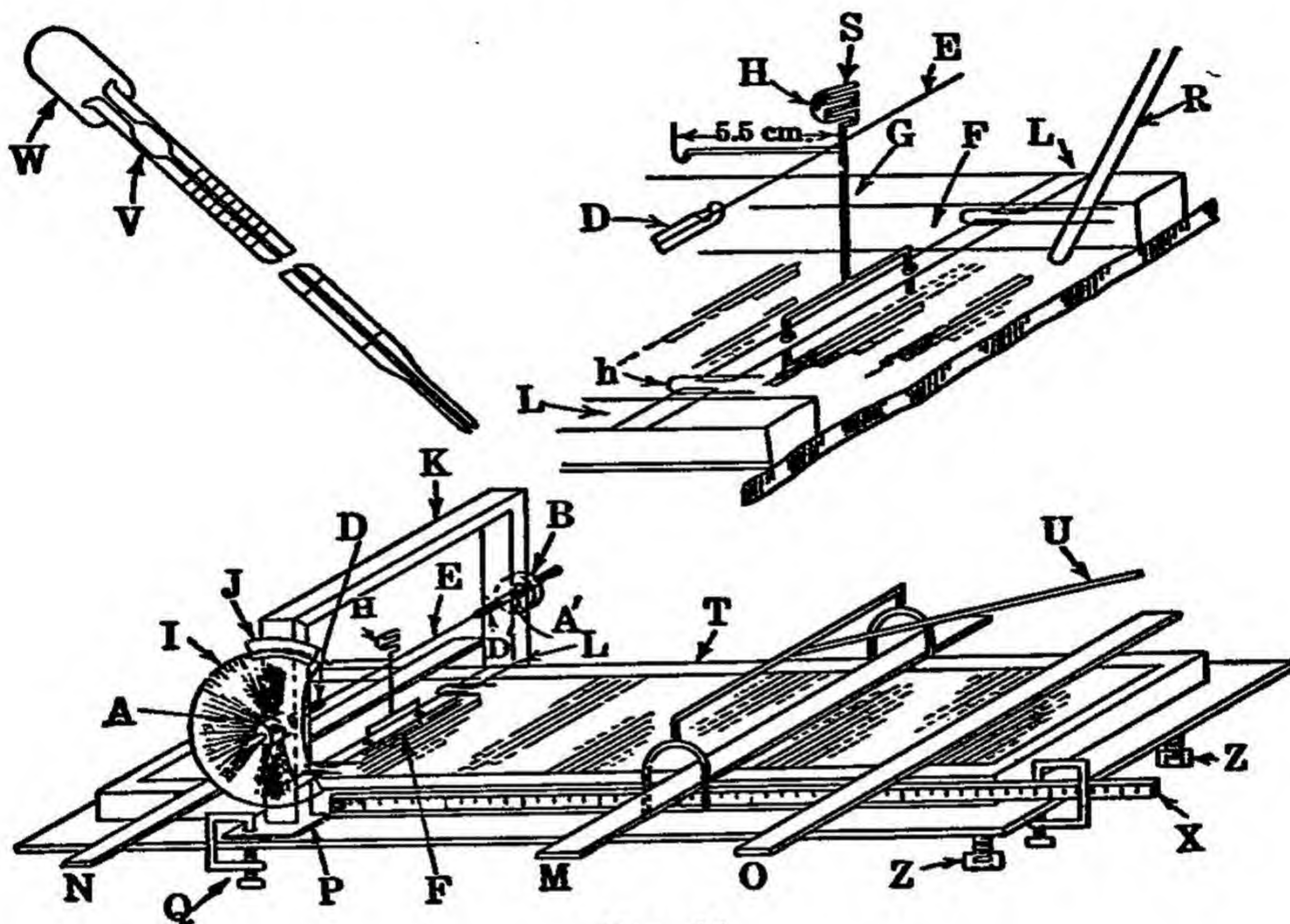


FIG. 31

in the axle to a depth of 1 or 2 cm.; a larger hole or well for the solder is drilled a little more than half way through the *side* of the axle 0.5 cm. from the end. The soldering is accomplished by heating the rod — never the wire — with a small flame. A graduate dial I is fastened to the other end of D by the bearing and setscrew A. A vernier J is clamped to the frame. It is well to be able to read the dial to  $\frac{1}{10}$  of a degree or its equivalent. (An azimuthal scale from an old transit is good but a radio dial will do.)

The micro balance G can be made of welded steel drill rod but 18% nickel silver wire about 0.03" diam. (obtainable from



Baker and Co.) soldered with silver solder is better. The dimensions are shown in the inset. The right angle distance from the hook for the calibrating weight to the torsion wire and to the float must be accurately known. The counter-balance S contains the same length of wire as does the lower arm. A mirror H is sealed to the coiled counterbalance in order to record the position of the float by means of a focusing light and scale (not shown). A notch is filed at the point of balance and the micro balance soldered to the torsion wire. It is then centered by means of the adjusting screws B and A.

The float F is of thin mica 0.02 to 0.04 mm. thick, 5 mm. wide and 12.0 cm. long. Two holes larger than the balance arms and 3.5 cm. from each end (i.e. 5 cm. apart) are punched in the float. Two other mica sheets are prepared 1.3 cm. long. The technique required for assembling will be described later. Three or four glass barriers of thick window glass  $30 \times 1.5$  cm. are also prepared and the sharp edges smoothed off with a file or a stone or wire gauze. The distance of the barrier from the float is read on the meter scales X, and the barriers moved by means of the holder U.

A micro pipette or a calibrated dropping pipette is necessary for the accurate measurement of the small quantities of solution introduced on to the surface of the water. The one shown in the inset, Fig. 31, has a reading error of  $\pm 0.0001$  cc. It is made from 0.5 mm. bore capillary tubing, and may be calibrated by measuring with a reading micrometer and by weight of benzene delivered between marks etched on the capillary. The bulb V in the glass is for safety only and the rubber W for convenience in filling, as the level of the liquid in the capillary is best controlled by tipping.

A glass protecting case with sliding doors in the front is advisable, for otherwise the surface is rather quickly contaminated by dust and vapors in the atmosphere.

#### OPERATION

**Cleaning and Paraffining.** In this work it is exceedingly important that the trough, float and barriers be entirely free from grease or any other contaminating substance, and the following precautions are necessary. The trough is cleaned under tap



water with fine emery cloth or by means of fine emery powder and a small rubbing block of wood until the trough becomes wet all over. The barriers are treated similarly and then cleaned with a chromic acid cleaning solution and then washed with hot distilled water. The cleaned trough is washed with a large quantity of boiling distilled water (2 or 3 liters) and if it does not dry in a short time it is dried in a warm place. While still hot both the barriers and sides and edges of the trough are coated with paraffin by means of a dilute (5%) solution of paraffin in pure benzene. This solution is conveniently painted on by means of grease-free cotton held in forceps. *From this point on the inside and sides of the trough must not be touched with the hands, and the barriers are to be handled by the ends only.* It is necessary to coat the trough while it is hot to get a good smooth application of paraffin — otherwise the glass barriers cannot be moved along easily.

**Adjustment of Float and Balance.** The trough is next set horizontal on the leveling screws Z (round head machine bolts are suitable) and the short mica pieces L (previously paraffined with the benzene solution) sealed with paraffin to the edges of the trough so that they extend inside a distance of 4 mm. and are 8 cm. from the end of the trough. This is done with a hot glass rod. The balance is then set in place and the trough leveled and filled to the brim with good distilled water from a still free from rubber or cork. The float, F, previously paraffined with the benzene solution, is put in place under the prongs of the torsion balance and the axis adjusted until the gaps are the same on each side; and these should be about 6 mm. A loop of fine, straight hair is sealed to a clean glass rod R (see inset) with paraffin, and the end of the loop washed with benzene and then a 10% benzene solution of good paraffin oil. This loop h is then sealed to the ends of the float and mica side-pieces by means of paraffin and a hot rod approximately 1 mm. in from the gap and of such length as to form a perfect semi-circle on the surface behind the float. The loop is then burnt off in front of the float by touching with a hot rod, and the other side fixed in the same manner. The float is then measured, the length being taken from points one half the distance between the ends of the semi-circle. For more accurate work a silk fibre may be substituted for the hair; the fibres are best handled on black velvet and must be straightened by washing



with hot water, dried under tension, and coated with mineral oil as with the hair. In any case the thin mica side-pieces are important as they do not form a meniscus with the surface of the water. It is well to coat with a thin layer of paraffin the top of the mica side-pieces at the end and similarly the tops of the ends of the float before putting them in position.

The light image on the scale and the dial are then adjusted to their respective zero points by means of A, A', and the scale. The balance is clamped down, and the meter scales X adjusted to give the distance of the barrier from the float.

The system is then tested for leaks by placing an oil film on the surface, talc is sprinkled near the loops, and the film compressed. The position of the float is of course held constant by turning the torsion wire dial. Movement of the talc indicates leaks. These may be corrected with a hot rod, care being taken not to burn the hair loops. The surface on both sides of the float is then swept clean with the barriers O and N. It is necessary to blow the last bit of contamination behind the float under the barrier N. These undesired films may be compressed into the ends of the trough and skimmed off with filter paper.

The balance is calibrated by means of a 10 mg. rider on the hook of the horizontal arm. The force is calculated as dynes per division on the dial and dynes per centimeter on the float. The surface is tested for contamination by decreasing the area tenfold, with the barrier M. If this decrease of area causes a total surface pressure of more than one dyne, the surface must be swept again or possibly the trough must be again cleaned. If the cleaning, paraffining and adjustment of float and hair have been carefully done this requirement will be met. Always move the barriers with the holder U, for any contamination of these is continually transferred to the surface.

**Experiment.** When the oil film is placed on the water surface, the molecules may be widely separated from one another, and be moving about on the surface like gas molecules in two dimensions; or they may be close together but lying down in the surface, and are generally not stacked together vertically, as in Fig. 30, unless they are pushed together by compressing the film. The film is then said to be "condensed."

The oil film is placed on the surface between the float F and



the barrier M with the micro pipette. An accurately measured volume of from 0.0500 to 0.0800 cc. of a freshly prepared 0.002 M solution of a fatty acid in purified benzene is a convenient amount for condensed films. After a few seconds the benzene will have evaporated and then the film is compressed and readings of the surface pressure taken, with the torsion balance, at various areas until the film becomes quite incompressible (up to about 50 dynes/cm.). Care must be taken to maintain the float at its zero position with respect to the barrier, and this is done of course by keeping the spot of light on a fixed mark on the scale. Obviously this applies to an expansion of the film as well; otherwise the float hairs may be broken off.

Use palmitic acid, stearic acid (and if desired oleic acid). Cerotic acid,  $C_{25}H_{51}COOH$ , is another good one to use. In fact any acid in this series, from a 12-carbon to a 25-carbon molecule, gives good results. Tristearin is especially instructive. (These substances may be obtained from the Eastman Kodak Co.)

The bulk density of palmitic acid at room temperature is about 0.845, of stearic 0.850, oleic 0.890, and tristearin 0.870 (or the densities of the acids may be measured; see Exp. 9 and Exp. 38). Assuming that the densities of the films are the same as the densities of the substances in bulk, calculate the thickness of the films by dividing the film volume by the film area. This will give the lengths of the vertically placed hydrocarbon chains. Also divide the film area by the number of molecules in the film to get the cross-sectional area per molecule as one looks vertically down on the film. Plot the cross-sectional area per molecule as abscissas, at various compressions, against the surface pressure in dynes/cm. as ordinates, and draw a straight line through the high pressure points to cut the abscissa axis and thus get the cross-sectional area per molecule (the intercept) for a condensed film at no compression. Compare this value for the different molecules and explain the results. This cross-sectional area increases with temperature. Langmuir and Adam and others have worked at  $12^{\circ}$ – $15^{\circ}$ , but good values, although somewhat larger than theirs, may be obtained at room temperature. Express the length of each molecule in cm., mm.,  $\mu$ ,  $m\mu$ , and  $\text{\AA}$  (Ångström units).

If the carbon atoms in stearic and palmitic acid molecules were arranged in a *straight* chain, with a distance of 1.54 Å between

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centers of adjacent carbon atoms, what would be the approximate expected length of these two molecules? The student should calculate from his *measured* lengths the angle between the bonds of the carbon atoms, assuming that the atoms are arranged in a zig-zag chain.

The student should by all means look up a discussion by Langmuir, "The Effects of Molecular Dissymmetry on Properties of Matter," pp. 525-46, in Alexander's *Colloid Chemistry*, vol. I, The Chemical Catalog Co., 1926, and follow the argument by which Langmuir shows when we are to expect the molecules to lie down in the surface, when they assume a stick-like shape and when they coil up into little balls. The argument is based on considerations of surface tension, interfacial tension, and a Boltzmann factor treatment, such as that developed in Exercise III.

#### REFERENCES:

- Taylor, Chap. IV.
- Rodebush, Chap. VIII.
- Millard, Chap. III.
- Adam, *The Physics and Chemistry of Surfaces*, Oxford Press.
- Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916); **39**, 1848 (1917); *Met. Chem. Eng.*, **15**, 468 (1916).
- Harkins, *J. Am. Chem. Soc.*, **39**, 354, 541 (1917).



## EXPERIMENT 13

### SPECTROMETRIC OBSERVATIONS

When a beam of light strikes a glass prism, such as that shown in Fig. 32, it is refracted, and because the angle of refraction varies with the wave-length, a beam of white light, or any composite beam, is spread out into a spectrum. This principle is applied in the spectrometer to the analysis of light rays and the determination of wave-length.

In Fig. 32, the angles  $i_1$  and  $i_2$  between the incident and emergent beams, respectively, and the perpendiculars to the prism faces, are known as angles of incidence, and the internal angles  $r_1$  and

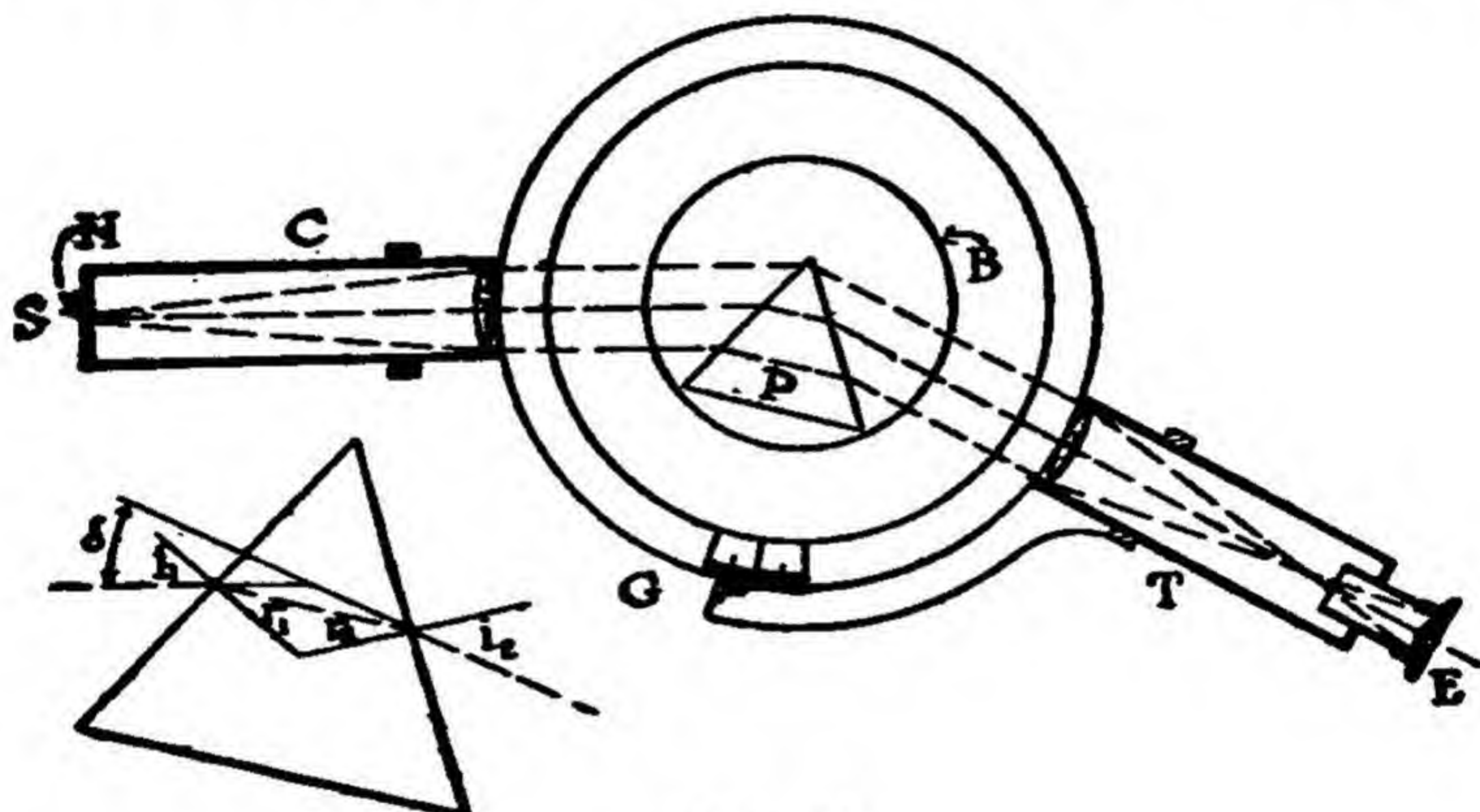


FIG. 32

$r_2$ , as angles of refraction. The angle of deviation is the angle between the incident and emergent rays, or geometrically,  $\delta = (i_1 - r_1 + i_2 - r_2)$ . It has been observed experimentally that there is a minimum angle  $\delta$  corresponding to a single angle of incidence. Since  $i_1$  and  $i_2$  may each be incidence angles, the only case in which  $i$  is single-valued is for  $i_1 = i_2$ . Hence this is the condition for  $\delta$  being a minimum.

The prism may be set with  $\delta$  a minimum for a known wave-length, for example, the *D*-line of sodium; then the angles of deviation of other lines may be determined without movement of



the prism. Since the angle of deviation is a continuous function of the wave-length  $\lambda$ , for a fixed prism position, if a plot of  $\lambda$  against  $\delta$  for several known wave-lengths be made, then the wave-length of other lines for which  $\delta$  is determined may be read directly from the curve.

#### EXPERIMENTAL

A plan of the spectrometer is shown in Fig. 32. Remove the telescope T from its clamps, and after focusing the eyepiece on the cross-hairs, focus the telescope for parallel rays by looking through it at some object several hundred yards away, and adjusting the length of the telescope tube until the image is sharply defined. When this adjustment is properly made there is no relative displacement of the cross-hair and the image when the eye is moved from side to side in front of the eye-piece E.

Replace the telescope on the stand, remove the prism P and with the telescope look through the collimator tube C at the slit H which is illuminated with a sodium flame S. Adjust the length of the collimator tube so that the slit is sharply defined in the telescopic field. The slit itself should be made as narrow as is compatible with good visibility. Now fix the prism in position, with its refracting edge parallel to, and nearest to the slit, and turn the telescope until the image of the slit falls on the vertical cross-hair or on the intersection of the two cross-hairs. The position of the collimator and telescope must be adjusted so that their axes are always perpendicular to the axis of rotation of the prism table and the table must be adjusted so that the refracting edge of the prism is always parallel to its axis of rotation. Rotate the prism back and forth, in the meantime following the image of the slit by turning the telescope, until the position of the prism is found where the image of the slit just stops moving in one direction and starts to move in the other. The prism table B is then clamped in this position. The angle of minimum deviation for sodium light is read on the circular scale G, with the aid of the reading lens and vernier.

Several other incandescent substances are placed before the slit and the angles of deviation determined for spectral lines of known wave-length. Construct a "spectrum map" by plotting the observed angles against the wave-lengths of the selected lines



given in the following table and drawing a smooth curve through the points.

TABLE IX

Element	Color	$\text{\AA}$
Sodium . . . . .	Yellow	5893
Potassium . . . . .	Red	7702
Thallium . . . . .	Green	5351
Strontium . . . . .	Violet	4607
Argon . . . . .	Violet	4228

The colored flames are produced by soaking pieces of asbestos in saturated solutions of the metal chlorides and heating with a hot gas flame, or by making a small chimney of asbestos cloth at the top of a Bunsen burner, soaking the asbestos with the salt solution, and letting the flame issue from the chimney. With some salts a better flame may be secured by letting the salt, in finely powdered form, fall through the flame. Argon and other gases to be studied are supplied in Plücker tubes, and are excited by the discharge from an induction coil.

After the construction of the spectrum map covering the range 4228–7702  $\text{\AA}$ , determine the wave-lengths of several of the more prominent lines in the spectra of lithium, calcium, strontium and barium chlorides.

Using a glass (not quartz) mercury vapor lamp, operated on a direct current line, determine the wave-lengths of the principal lines in the spectrum of mercury vapor. (Mercury vapor lamps may be obtained from chemical supply companies, or a simple lamp which is easily made from pyrex glass, and which does not require an evacuating pump, is that described by Vincent and Biggs, *J. Sci. Instruments*, 1, 242 (1924)). Examine the spectrum of a cadmium arc by using two cadmium metal rods and a direct current (from motor generator). Repeat with two iron rods and note the enormous complexity of the spectrum of an iron arc.

Determine the wave-lengths of the principal lines in the spectra of the glowing gases, hydrogen, helium, neon, argon, krypton and xenon. The lines of the visible hydrogen spectrum belong to the Balmer series. The wave-number\*  $\nu_0$  of these lines is given by the

\* The wave-number  $\nu_0$  is  $1/\lambda$ , where  $\lambda$  is expressed in cm.



Balmer equation,

$$\nu_0 = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right)$$

where  $R$ , the Rydberg constant, equals 109,678 (109,677.69  $\pm$  .06) and  $n$  is 3, 4, 5, 6, respectively, for the  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ , and  $H_\delta$  lines. If we put  $n = \infty$ , the limiting frequency or head of the series is obtained, namely,  $\nu_0 = R/4$ . Obtain the wave-number of the  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ , and  $H_\delta$  lines from your spectrometric observations and compare with those calculated from the Balmer equation. The  $H_\epsilon$  line is slightly beyond the range of the spectrum map, but its wave-length can be estimated. What are the Lyman, Paschen and Brackett series?

Study the absorption spectrum of potassium permanganate solution by placing a glass vessel of flat sides in front of the spectro-scope slit, with a piece of asbestos board between the vessel and a frosted electric light bulb (60-75 watts). With a cork borer cut a hole 1-1.5 cm. in diameter in the asbestos opposite the slit, and place 100 cc. 0.4 per cent solution of potassium permanganate in the vessel. Examine the light passing through the solution and find the angular deviations of the outside edges of the red and violet bands. Dilute the solution by removing 50 cc. with a pipette and adding 50 cc. of distilled water. Continue the dilution, in each case observing the angular deviation of the outside edges of the bands, until a continuous spectrum is obtained. Determine the wave-length of the green lines which appear at a certain dilution. Make on the same piece of graph paper a series of drawings of the absorption spectra, showing the position (wave-length) of the band edges at the various dilutions.

REFERENCES:

- Taylor, Chap. I.
- Rodebush, Chap. XV.
- Getman and Daniels, Chaps. V, XXI and XXIII.
- Millard, Chap. XV.
- Findlay, Chap. I.
- Eucken, Jette and LaMer.
- Ruark and Urey, *Atoms, Molecules and Quanta*, McGraw-Hill.



## EXPERIMENT 14

### POLARIMETER; REACTION VELOCITY CONSTANT

The fundamental principle on which the various types of polarimeters operate is the same, although there are differences of detail in the construction of such instruments. It will be assumed in the present description that a Schmidt and Haensch half-shadow instrument of the Lippich type is available.

The polarimeter consists essentially of two Nicol (Iceland spar) prisms, P the polarizer and A the analyzer (in Fig. 33), mounted near opposite ends of a long brass tube. The analyzer A is fixed to the center of a circular dial so that it may be turned about an

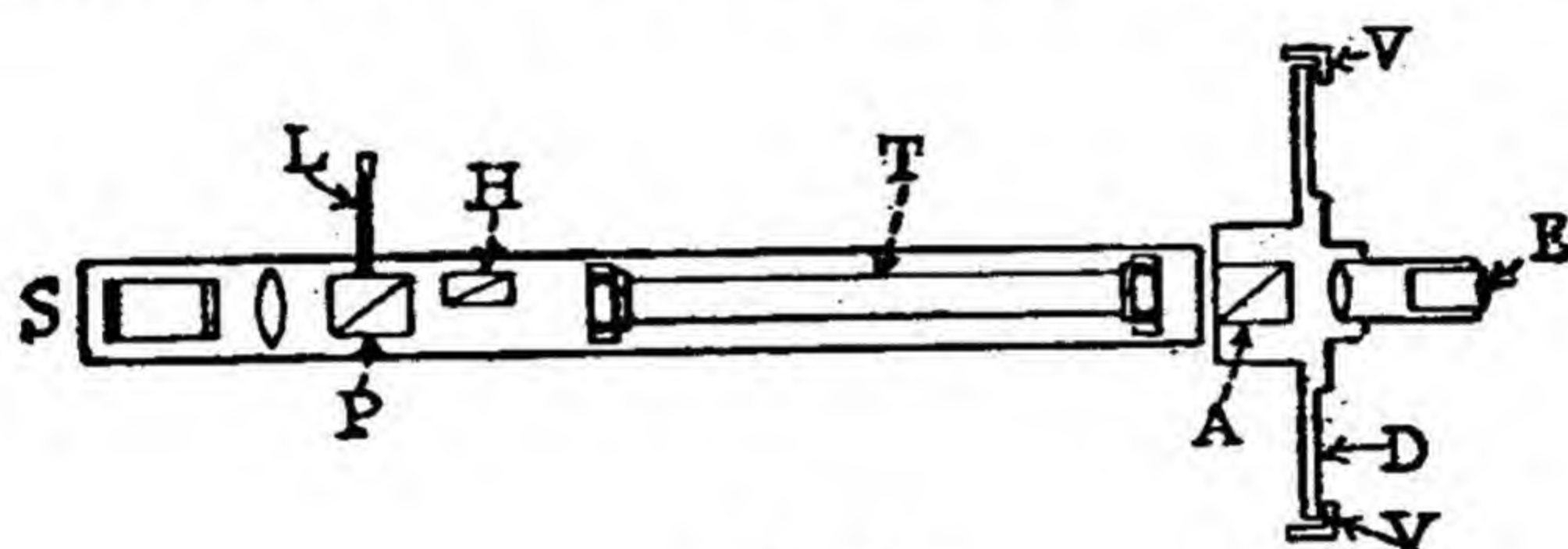


FIG. 33

axis parallel to the long tube, through any desired angle measured on the dial scale D, provided with vernier reading devices V, V. When light from the source S is allowed to pass through the polarizer P, the light is plane polarized, that is, only light made up of vibrations in one plane is transmitted by the prism P. When this beam of polarized light passes down the tube, the prism A can be rotated into two positions, each  $180^\circ$  apart, which permit the polarized light to pass through with practically undiminished intensity, and into two other positions,  $90^\circ$  from the first two, where complete extinction of the beam is produced, when observed through the focusing eye-piece E. In intermediate prism positions the light is transmitted with intermediate intensities.

Let us suppose that the analyzer prism A is turned to a position which gives minimum transmission. If now a quantity of a



so-called "optically active" substance with the power of rotating or twisting the plane of polarized light is introduced between P and A, observation through the eye-piece E will show that minimum transmission is no longer present. But rotation of A through an angle measurable on the dial scale will restore the original condition of darkness. This angle is a measure of the rotating power or optical activity of the substance. When it is necessary to turn the analyzer in a clockwise direction, the substance is said to be dextro-rotatory, and when anti-clockwise, levo-rotatory. There are, of course, two angles through which the analyzer may be turned to reach the end-point, one the angle  $\theta$  and the other  $180^\circ - \theta$ . The smaller one of them is called the angle of rotation, and is taken as a basis of designation of the rotation as levo- or dextro-.

To determine the angle of rotation in the manner just described is not an easy matter because of the difficulty of matching the degree of darkness of one setting with a previous one, especially when the matching has to be done by memory. One method for avoiding this difficulty consists in placing a small Nicol prism which covers just half the field at H. The prism P is turned so that its axis makes a small angle with that of H, say  $2^\circ$ . Now if the analyzer A is turned so that its axis is at right angles to that of P, then the lower half of the field appears dark and the upper half perceptibly brighter. If A is then turned through  $2^\circ$  so that it is now at right angles to the axis of H, then the upper half of the field is dark and the lower bright. If A is turned through only  $1^\circ$ , each half of the field is illuminated to the same extent. When an optically active substance is then placed in position in the tube, and the plane of polarized light thereby rotated, the analyzer A may be turned through such an angle that the two halves of the field again match, and this angle is the angle of rotation. The lever L controls the angle of setting for the prism P, and by manipulation of this lever the sensibility of the instrument may be adjusted, but, once set, it should be left undisturbed. The angle of setting should be small for clear solutions, generally  $2^\circ$ - $4^\circ$ , but, for turbid or dark colored solutions, it should be made larger.

The optically active substance is introduced into the glass tube T, provided with circular glass end plates held in position with rubber washers and screw caps. The angle of rotation depends



somewhat on the temperature, and container tubes may be jacketed for circulation of a stream of water at a constant, known temperature. In the present experiment, however, we shall work at room temperature. The light from source *S* should be monochromatic, since the rotation effect is greater with short than with long wave-lengths. It is becoming increasingly the custom to employ the green line (5461 Å) of the mercury vapor arc in standard polarimetric work, although much of the data in the literature has been collected while using the *D*-line (5893 Å) of a sodium flame. In the present experiment, a very satisfactory yellow sodium flame may be obtained by heating a piece of pumice stone soaked in sodium chloride solution with a hot Meker burner flame, or by heating a small alundum crucible of the proper porosity (R.A. 360) about one-third full of sodium chloride, to which some sodium chromate has been added to lower the temperature of fusion. The sodium flame should be placed far enough away (10–15 cm.) to prevent injury to the instrument, and it is well to provide an asbestos shield with an observation hole cut through it. A small chamber filled with a 9 per cent aqueous solution of potassium dichromate acts as a light filter, and helps to render the transmitted light more nearly monochromatic. A sodium vapor lamp, most excellent as a light source for polarimetric work (Sodium Lab-Arc) operating on an ordinary 115 volt 60 cycle electric light current, is made by the G. E. Vapor Lamp Co., Hoboken, N. J.

The degree of rotation produced by an optically active substance placed in the path of the polarized light depends not only on the *nature* of the substance itself but also on the *length* of the column and in the case of *solutions* of optically active solutes, it depends on the concentration. In comparing the rotatory power of one substance with that of another, it therefore becomes necessary to define the conditions of comparison. A length of 10 cm. is taken as the standard length of column. From the observed angle of rotation  $\alpha$ , the so-called "specific rotation"  $[\alpha]$  is calculated for a pure liquid by the equation

$$[\alpha] = \frac{\alpha}{l \cdot d}$$

where  $d$  is the density of the substance, and  $l$  the length of the



column in decimeters. In the case of an optically active solute in solution, the specific rotation is given by the equation

$$[\alpha] = \frac{100 \cdot \alpha}{l \cdot c}$$

where  $c$  is the number of grams of the solute in 100 cc. of solution. If the concentration is expressed as grams per 100 grams of solution, then the equation becomes,

$$[\alpha] = \frac{100 \cdot \alpha}{l \cdot d \cdot g}$$

where  $d$  is the density and  $g$  the number of grams of solute. The specific rotation multiplied by the molecular weight of the substance gives the molecular rotation,  $M[\alpha]$ .

#### EXPERIMENTAL

(a) Fill the tube T with distilled water and find the zero reading on the scale D. Take the average of at least 10 settings, approaching the zero from the left in half the readings, and from the right in half. If this does not correspond to the zero mark on the scale, adjustment should be made with the set screws, by means of which the position of the analyzer A may be rotated slightly with respect to the scale D. Or, the deviation of the observed zero from the scale zero may be noted, and this constant correction made in all further readings. In making the readings, the slow-motion adjustment should be brought into play, with a set screw provided for that purpose.

Using a sodium flame, determine the angle of rotation (at room temperature) of solutions containing 10 grams and 20 grams of cane sugar per 100 cc. of solution. In each case take the average of 10 settings. What is the average deviation from the mean for a single observation? (See Exercise II.) Calculate the specific and the molecular rotation, for each solution.

(b) Determine the velocity of inversion of cane sugar in the presence respectively of 0.5 M acetic acid and of 0.5 M chlor-, dichlor-, and trichlor-acetic acids. Weigh 20 g. pure cane sugar into a 100 cc. volumetric flask; dissolve the sugar in 0.5 M acetic acid and dilute to the mark, thus obtaining a 20 per cent sugar content in a 0.5 M acid solution. Prepare the chlor-, dichlor-, and



trichlor-acetic acid solutions in the same manner. Fill four glass polarimeter tubes (T in Fig. 33), No. 1 with some of the acetic acid sugar solution, No. 2 with the chlor-, No. 3 with the dichlor-, and No. 4 with the trichlor-acetic acid sugar solution. Take initial readings with the polarimeter, and then hang the four tubes in a water thermostat kept at 25°. Make polarimeter readings at regular intervals and let the tubes remain in the thermostat for 24 hours for a final reading.

Plot the observed angle of rotation against time for the four solutions. Assuming that it is the hydrogen ion which catalyzes the inversion, what is the degree of ionization of the acetic, the chlor-, and dichlor- relative to that of the trichlor-acetic acid?

The inversion of cane sugar,



might be expected to be a bimolecular reaction, but because the concentration of the water remains practically constant from the beginning to the end of the reaction, it really follows the monomolecular reaction law. From your data calculate the reaction velocity constant for the trichlor-acetic acid solution at the various time intervals. Instead of using the equation (compare Exercise III)

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

where  $k$  is the velocity constant,  $t$  the time,  $a$  the original concentration of cane sugar, and  $a-x$  the concentration at time  $t$ , the following equation may be employed in which the concentrations are expressed in terms of angles of rotation.

$$k = \frac{1}{t} \ln \frac{\alpha_i + \alpha_f}{\alpha + \alpha_f}$$

where  $\alpha_i$  is the initial angle of rotation,  $\alpha_f$  the final angle after complete inversion, and  $\alpha$  the angle at time  $t$ . This alternative equation is legitimate because  $a$ , the original concentration of sugar, is proportional to the total change in angle when all of the sugar is inverted, namely  $\alpha_i - (-\alpha_f)$ , since the initial angle is on the + side of zero reading and the final angle is on the - side. Similarly  $x$ , the concentration which has undergone inversion at



any time  $t$  is proportional to  $(\alpha_i - \alpha)$ . Hence  $(a - x)$  is proportional to  $(\alpha_i + \alpha_f) - (\alpha_i - \alpha)$  which reduces to  $(\alpha + \alpha_f)$ .

**REFERENCES:**

Getman and Daniels, Chaps. V and XIV.

Millard, Chap. X.

Findlay, Chaps. V and XII.



## EXPERIMENT 15

### MINIMUM BOILING MIXTURE; ABBÉ REFRACTOMETER

Binary liquid mixtures (completely miscible) may be divided into three classes: (1) those in which the boiling points and vapor pressures of all possible mixtures lie intermediate between those of the two components; (2) those which exhibit a maximum in their boiling point curves or a minimum in their vapor pressure curves; and (3) those which exhibit a minimum in their boiling point curves or a maximum in their vapor pressure curves. In the following experiment a binary mixture of the third class is studied. Benzene and methyl alcohol are mixed together in various proportions, and refluxed. At the different boiling points, samples of the condensed vapor (in the reflux condenser) and of the liquid (represented by the residue in the distilling flask) are taken and the compositions of both determined with an Abbé refractometer. From the data a complete boiling point-liquid-vapor composition diagram is constructed.

#### EXPERIMENTAL

Figure 34 shows the apparatus. It consists of a 250 or 500 cc. flask provided with two necks. Through one of these the thermometer is inserted, and through the other one a long reflux condenser tube A. A convenient form of replaceable water-jacket, with carefully bored rubber stoppers, is shown in the figure. The lower end of the condenser tube is made into a little cup, B, by closing the end and leaving a hole in the side of the tube, as indicated in the figure. During the boiling process this cup is inverted, hole down. When one desires to take a sample of the vapor condensing in the reflux tube, the tube A is turned through an angle of  $180^\circ$  in the rubber stopper in the neck of the flask, so that a few drops of reflux liquid collect in the cup.

Place a known mixture of benzene and methyl alcohol in the apparatus and heat gradually with a small flame or electric heater until it comes to a constant boiling point. Now the vapor above



the boiling liquid and in the reflux tube is very nearly in equilibrium with the solution. Remove the flame to a safe distance, and turn the cup B so that the reflux liquid returning to the flask is caught. Take out the thermometer, insert a long-stemmed, fine-pointed pipette through D and withdraw a few drops of the

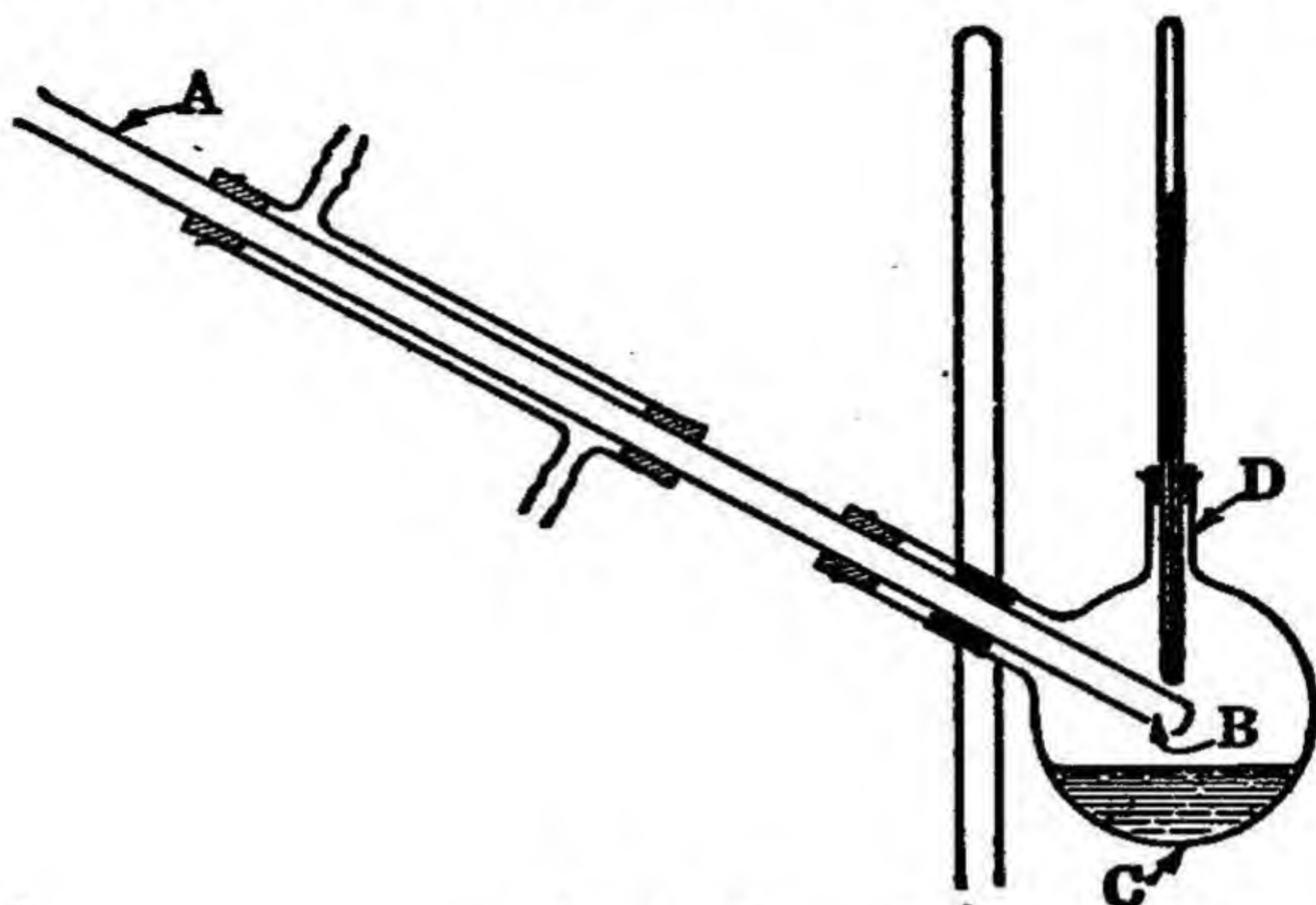


FIG. 34

liquid from the cup by sucking. This is to be kept in a small labelled sample bottle. Immediately take a similar sample from the liquid in the flask, using a second pipette, and store in another labelled bottle.

Then add either methyl alcohol or benzene to the flask, replace thermometer, invert cup B, and heat again to boiling. Continue the sampling as before for 15 to 20 different compositions of the liquid over the range of 95 mol per cent of  $\text{CH}_3\text{OH}$  to 95 mol per cent of  $\text{C}_6\text{H}_6$ , by making proper adjustments of the relative amounts of the two substances. The boiling points should of course be carefully noted and recorded just before every sampling. The small sample bottles, or small test tubes or small vaccine tubes, provided with corks, should be arranged in a systematic order on the laboratory table so as to be ready when needed. They may be labelled  $V_1, V_2, V_3, \dots$  for the samples of condensed vapor and  $L_1, L_2, L_3, \dots$  for the samples of the liquid taken from the flask. The samples may be very small, three or four drops being quite sufficient.

The samples collected are now to be analyzed by means of the Abbé refractometer (see Fig. 36). To be able to do this one must



know how the refractive index changes with the composition of the mixtures. This is accomplished by taking nine small bottles, placing them in a row, and adding from a 1 cc. pipette, graduated in 0.01 cc., 0.100 cc. of benzene, previously cooled to 20.0° C. in a bath, to the first bottle, 0.200 cc. to the second bottle, 0.300 cc. to the third bottle, and so on. The pipette is cleaned by blowing air through it, and then methyl alcohol, likewise cooled to 20.0° C., is added, 0.900 cc. to the first bottle, 0.800 cc. to the second, 0.700 cc. to the third, etc., so that each bottle thus contains 1.00 cc. of a mixture of definite amounts of benzene and methyl alcohol. Taking the density of benzene at 20.0° C. to be 0.879 and that of methyl alcohol to be 0.792, calculate the composition of each mixture in terms of mol per cents. Now determine the refractive index of these mixtures and also of the two pure liquids at 20.0° C. and plot the refractive index against the composition in mol per cents. By drawing a smooth curve (one that has no sharp breaks or sudden changes in slope) through these points the mol percentage corresponding to any refractive index can be read off directly.

Determine the refractive index, at 20.0° C., of each of the samples collected and read off its composition. Finally plot the boiling temperature of each sample against the composition of the vapor and liquid phases expressed in mol per cents and draw smooth vapor- and liquid-phase curves. Describe, in terms of the diagram, the changes that take place in the two mixtures boiling at 60° when they are fractionally distilled.

#### ABBÉ REFRACTOMETER

When a ray of monochromatic light passes from a less dense to a more dense medium, it is bent or refracted towards the normal. If we let  $i$  be the angle of incidence, that is, the angle between the direction of the ray of light and the normal to the surface between the two media, and let  $r$  be the angle of refraction, then the law of refraction gives us the relation

$$\frac{\sin i}{\sin r} = \frac{N}{n}$$

where  $n$  and  $N$  are the indices of refraction of the less dense and the more dense media, respectively. When the ray just grazes the

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surface between the media,  $i$  is a maximum and is equal to  $90^\circ$ . Since  $\sin 90^\circ = 1$ , the refractive index of the less dense medium is then given by  $n = N \sin r$ .

In the Abbé refractometer the more dense medium consists of a right-angled glass prism ABC (Fig. 35). The less dense medium consists of a layer of the liquid under investigation placed in contact with the hypotenuse face AB. The following paragraph is quoted from Findlay, *Practical Physical Chemistry*, pp. 94-5, 4th Ed. Figure 35 is also from this source.

"... a ray of monochromatic light passing through the liquid and entering the prism at grazing incidence, will emerge from the face AC perpendicular to that face, provided  $n = N \sin A$ " (that is, when  $r = A$ ). "For any other value of  $n$ , however, the ray of light will emerge at an angle to the face AC, less than a right angle, and in order that the ray may be brought parallel with the axis of the telescope, T, the prism must be rotated through an angle  $\alpha$ .

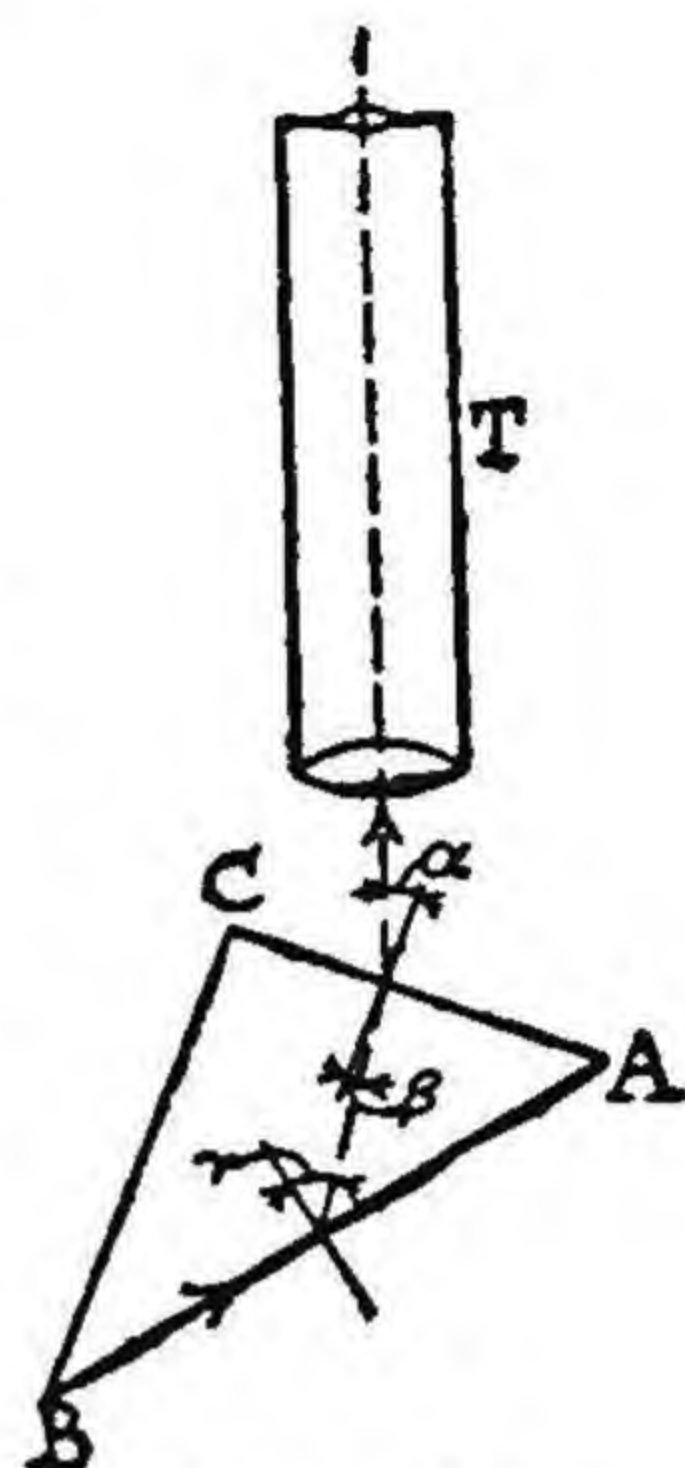


FIG. 35

By determining the value of the angle of emergence,  $\alpha$ , the refractive index of the liquid,  $n$ , can be calculated from the relations:  $N = \frac{\sin \alpha}{\sin \beta}$ ;  $\beta + r = A$ ;  $n = N \sin r$ . By eliminating  $\beta$  and  $r$ , we obtain  $n = \sin A \sqrt{N^2 - \sin^2 \alpha} - \cos A \sin \alpha$ ."

The instrument is shown in Fig. 36. In carrying out a determination the telescope and prism arm are swung away from the operator so that the upper prism is in a horizontal position and a drop or two of the liquid under investigation is placed on the prism. The lower surface is then turned over and clamped. The telescope and prism arm are then swung back to the stop and the mirror is adjusted so that light from a window in front of the instrument is sent into the telescope. The eye-piece is focused on the cross-wires and the reading lens on the scale; on moving the prism arm a position can now be found where the lower part of the field is dark and the upper part light. In general, the border-line will be found to be colored, due to the fact that white light and not monochromatic light is being used (the scale readings are for the D-line of sodium). This is corrected by turning the



milled screw-head on the telescope, which operates the "compensator," consisting of two prisms which rotate in opposite directions and so form a system of variable dispersion, until the colored fringe disappears and the light band shows a sharp edge. The prism arm is now moved until this edge just crosses the intersection of

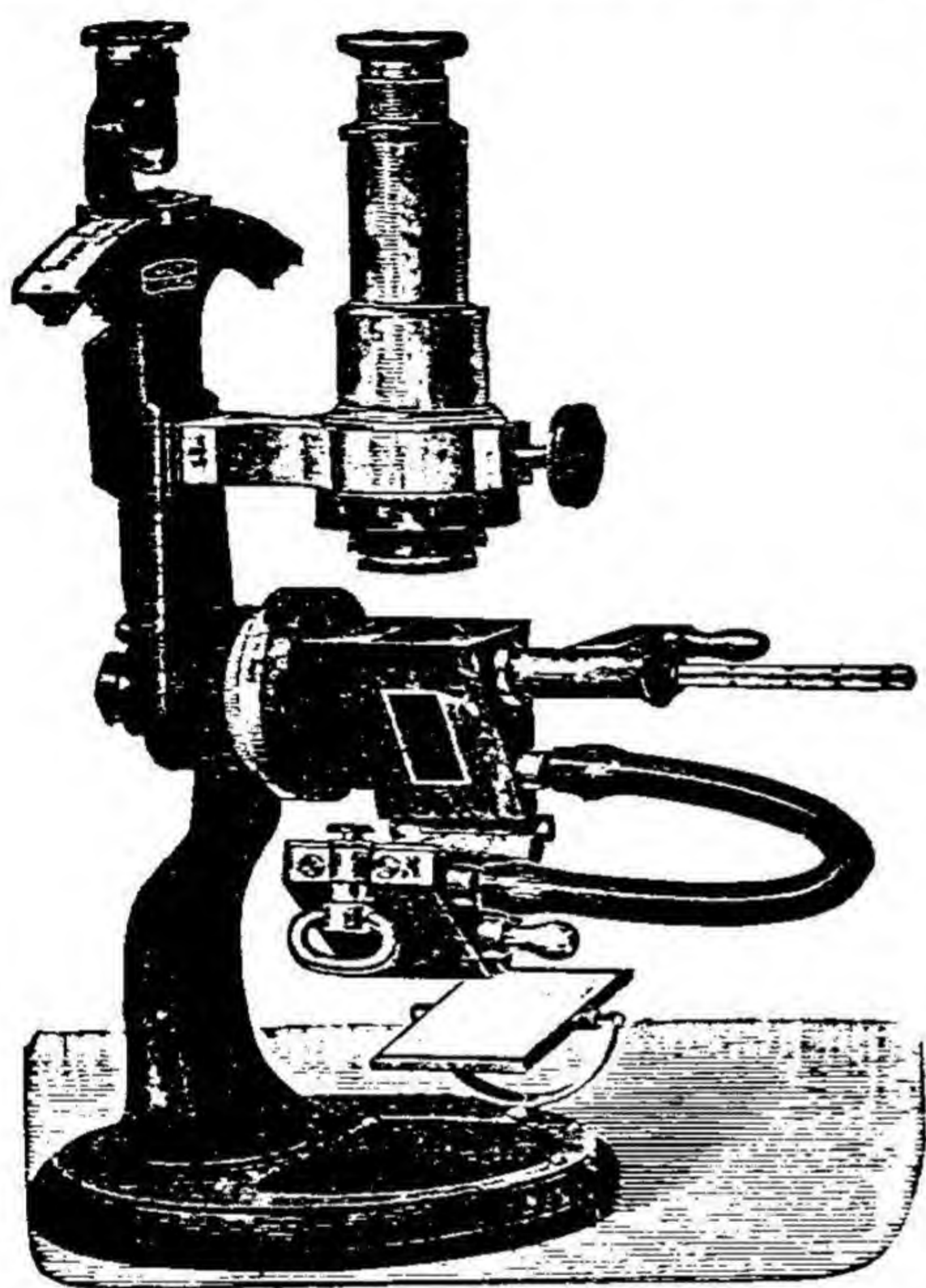


FIG. 36

the cross-wires; the refractive index is then read off on the scale, as the scale is graduated directly in values of the refractive index instead of in degrees, estimating the last figure to one-tenth of a scale division. The reading lens should be turned so that the inner reflecting surface of the tube helps to illuminate the scale.

As soon as possible the liquid should be removed from the faces of the prisms by means of a swab of absorbent cotton soaked in ether or ether-alcohol, the swab being renewed two or three times. In the above experiment, where mixtures of benzene and alcohol are used, the swabbing liquid

may be dispensed with. *Particular care should be exercised that the surface of the soft glass of the upper prism is not scratched; lens paper or absorbent cotton only should be used.*

The accuracy of the refractive index scale is checked by means of a small test piece of glass supplied with the instrument. This test piece has two polished surfaces at right angles; the larger face is attached to the upper prism by means of a small drop of a liquid of high refractive index, such as monobrom-naphthalene, in such a position that the ground end of the piece is directed toward the mirror. The lower prism must first be slipped off its hinge. In a poor light the polished end may be directed toward the mirror, the light being dispersed by means of a piece of tissue paper or lens paper.



Set the prism arm so that the reading corresponds with the refractive index etched on the test piece and by means of the compensator obtain a sharp colorless edge between the light and dark fields in the telescope. If this edge coincides with the intersection of the cross-hairs, the instrument is in proper adjustment; if it is not, loosen the two set screws which keep the prism box in a fixed position relative to the prism arm, move the prism box until coincidence is secured, and fasten the set screws again. Instead of making this adjustment, however, it is more convenient to use the difference between the reading in the telescope, when the test piece is used and the prism arm is moved until the edge between the light and dark fields coincides with the intersection of the cross-hairs, and the correct value of the refractive index of the test piece as a constant correction to be applied to all readings.

In case the lower prism is so fastened that it does not slip off its hinge, set the instrument upon a box in front of a window and adjust it so that the face of the upper prism is horizontal and the telescope is pointing slightly downward toward the student. The test piece may now be used as before, the light, however, coming directly to it from the window instead of first being reflected by the mirror. The relative positions of the light and dark fields will be reversed but this does not affect the readings in any way. The instrument may be used in this position throughout the experiment, an important advantage being that the telescope and prism arms need not be moved at all when the samples are being exchanged.

The temperature of the prisms should be kept constant by circulating water through the metal jackets surrounding the prisms (the thermometer having been inserted into place beforehand). This is conveniently done by siphoning water kept at the constant temperature from one large beaker to another at a lower level, the flow of water being regulated by means of a screw clamp on the rubber connections.

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- Taylor, Chap. X.
- Rodebush, Chaps. VII and XIII.
- Getman and Daniels, Chaps. V and VII.
- Millard, Chap. V.
- Findlay, Chaps. V and XIX.
- Earl H. Brown, *J. Chem. Ed.*, 9, 1114 (1932).
- Collins, Morrison and Stone, *ibid.*, 10, 749 (1933).



## EXPERIMENT 16

### FRACTIONATING COLUMN EFFICIENCY

By drawing illustrative material from the vast amount of recorded work on the fractional distillation of mixtures of volatile liquids, some very instructive experiments could be devised. We have already described, in Exp. 15, an analytical method (using a refractometer) for constructing the boiling point-composition diagram for the azeotropic mixture methyl alcohol-benzene. In the present experiment we shall describe a very simple scheme involving a graphical method, for comparing the efficiency of *fractionating columns*, or *still-heads*.

In the ordinary set-up of fractionating flask and condenser, employed by the organic chemist in his laboratory manipulations, we may call that portion of the flask below the vertical column the *boiler*, and call the vertical column, up to the point where the vapors enter the condenser, the *still-head*. At the exit end of the condenser there is generally located a *receiver*. The mixture of volatile liquids to be separated is placed, of course, in the *boiler*, and is generally boiled at atmospheric pressure, although exactly the same principles are involved at a reduced pressure. These general principles, underlying the theory of fractional distillation are as follows:

Let us limit our considerations to a 2-component mixture, and suppose that the mixture is not azeotropic. In the present experiment we shall work with a mixture of benzene and toluene. It happens that this mixture is almost "ideal" in its behavior, and follows Raoult's law fairly well. If we suppose that the benzene is present in larger amount and is thus to be called the *solvent*, then according to Raoult's law

$$p_b = p_b^0 \cdot N_b \quad (1)$$

where  $p_b$  is the pressure of the vapor of benzene in equilibrium with the mixture,  $p_b^0$  is the vapor pressure of pure benzene at the same temperature, and  $N_b$  is the mol fraction of the benzene. The same



relationship may be stated for toluene, the solute, but when stated for a solute it is known as Henry's law:

$$p_i = p_i^0 \cdot N_i \quad (2)$$

The total pressure of the vapor in equilibrium with the liquid mixture is  $(p_b + p_t)$ , and at the boiling point of the mixture is, of course, equal to the atmospheric pressure. If the vapor pressures of the two pure liquids are known over the boiling point range, from  $80^\circ$  for benzene to  $111^\circ$  for toluene, the composition of the vapors for various compositions of the liquid mixture can be calculated by Equations 1 and 2 and the boiling points plotted against liquid and vapor composition; as in Fig. 37. In general such a plot of

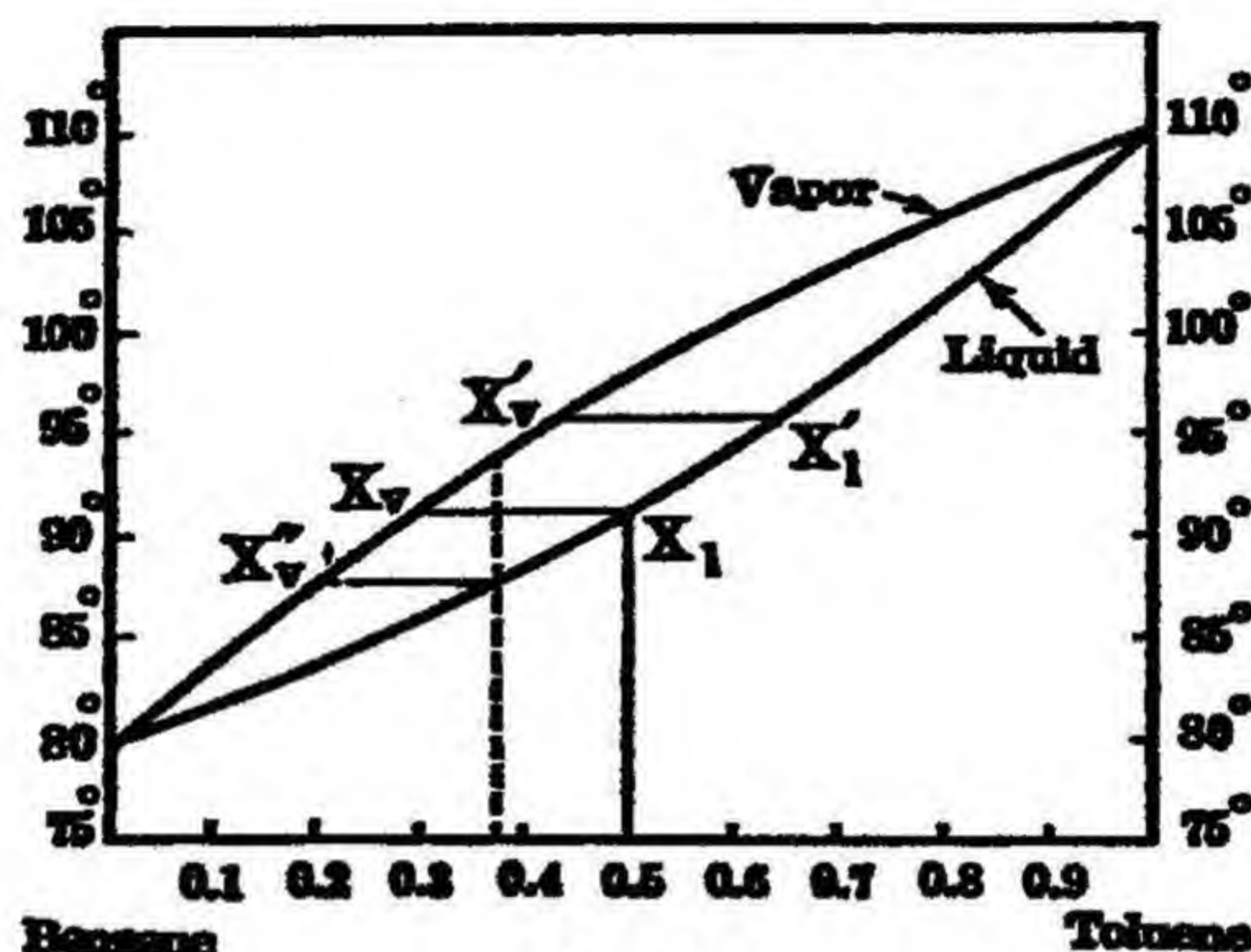


FIG. 37

calculated data would not agree at all well with a plot of actual experimental data, because of the failure of Raoult's and Henry's laws. In this particular case, however, with benzene and toluene, the agreement is fair.

The compositions may be conveniently plotted in terms of mol fractions. The lower curve gives the composition of the liquid, the upper of the vapor. If a 50-50 mol mixture of benzene and toluene is put in the boiler flask and boiled, the composition of the first vapor to come off is  $x_1$ , much richer in benzene, the more volatile component, than the liquid. On continued boiling the liquid becomes poorer and poorer in benzene, and richer and richer in toluene, the composition drifting up the curve to, let us say,  $x'_1$ . If the vapors coming off during this interval are condensed and



collected, the resulting condensed liquid will have a composition the average of  $x_v$  and  $x_v'$ , namely about 0.37 mol toluene and 0.63 mol benzene, much richer in benzene than the starting liquid. If now this liquid is boiled, the first vapors that come off will have the composition  $x_v''$ . Thus, by the usual scheme of successive fractional distillation, the mixture can eventually be fairly well separated into its two constituents.

It is the function of an efficient still-head to save much of the time and labor required for such a tedious scheme of separation. A good still-head is different from the very inefficient still-head of an ordinary fractionating flask in two respects. (1) Not only can separation of the differently volatile constituents be achieved by *evaporation*, during which the more volatile substances escapes more easily, but also by *condensation*, during which the less volatile substance condenses more easily. In the ordinary fractionating flask little condensation occurs until the mixed vapors have passed out of the still-head into the condenser, where there is then no chance of obtaining any further separation, since everything that enters the condenser, in the usual arrangement, passes on to the receiver. However, in a good still-head, separation by condensation plays an important part. (2) Also in a good still-head, *repeated* evaporation and condensation are made to occur.

These two effects, (1) and (2), may be embraced by another manner of statement. To obtain efficient separation, there must be a good deal of mixing and intimate contact between the hot rising vapors and the cold condensed liquid trickling back toward the boiler, so that *equilibrium* will be attained between vapor and liquid at the various points throughout the length of the still-head. In this state of affairs, the warmer rising vapors will be robbed continuously of their less volatile component by condensation, so that the more volatile component passes on up the column; and conversely, the cooler descending liquid is continuously having its more volatile component boiled out by evaporation, so that the less volatile component passes on down the column, back to the boiler.

For illustration, let us take the modified Young evaporator still-head, shown in Fig. 38. The column consists of a series of bulbs, B, three or more. Resting on the bottom of these bulbs, but *not sealed on*, are inverted test tubes, flared out into a funnel



shape at the bottom, and with two holes, H, at the top; and resting on these test tubes, are inverted tubes with flat tops, T. The vapor from the boiler passes up through a funnel, out the two holes H, down and up again, and finally enters the next bulb. The cooler condensed drippings from an upper bulb pass between the funnel and the bulb wall, fall upon the hot top T of a lower bulb and are partially re-vaporized. The warm vapors, issuing from H, strike the relatively cool top T and are partially condensed. The condensed liquid traveling down and the vapors rising up are brought into very intimate contact both in this way, and by a turbulent, eddying motion, at many points in the still-head. In an *ordinary* fractionating flask column, the rising vapors are pretty well channeled up the center of the tube, and the liquid runs down the walls; hence very little intimate mixing and contacting result.

**Graphical Method for Showing Efficiency of Still-Head.** If the still-head were 100% efficient,

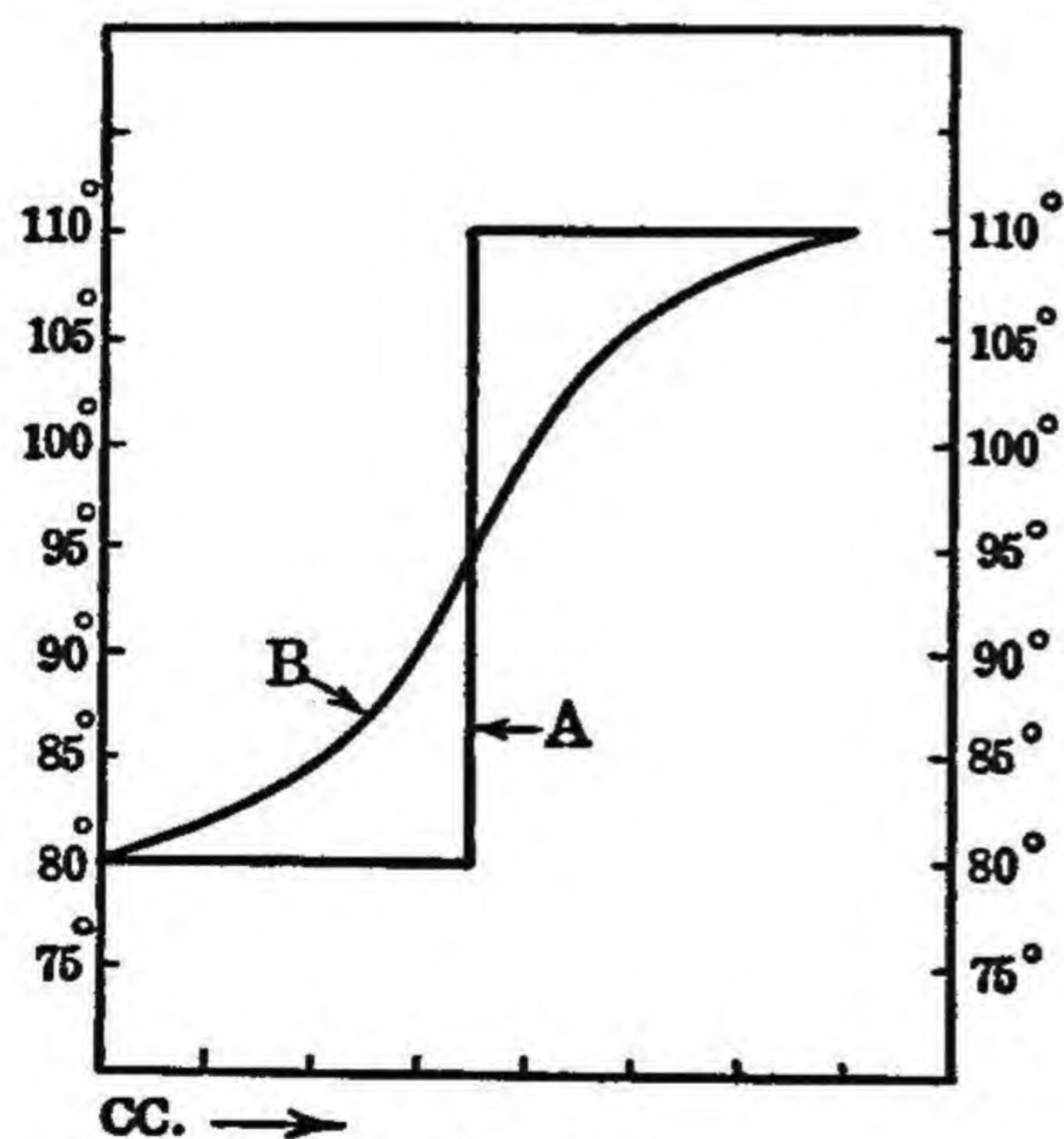


FIG. 39

less volatile constituent, and remain constant while the toluene is boiling over. With a very inefficient still-head a curve similar to

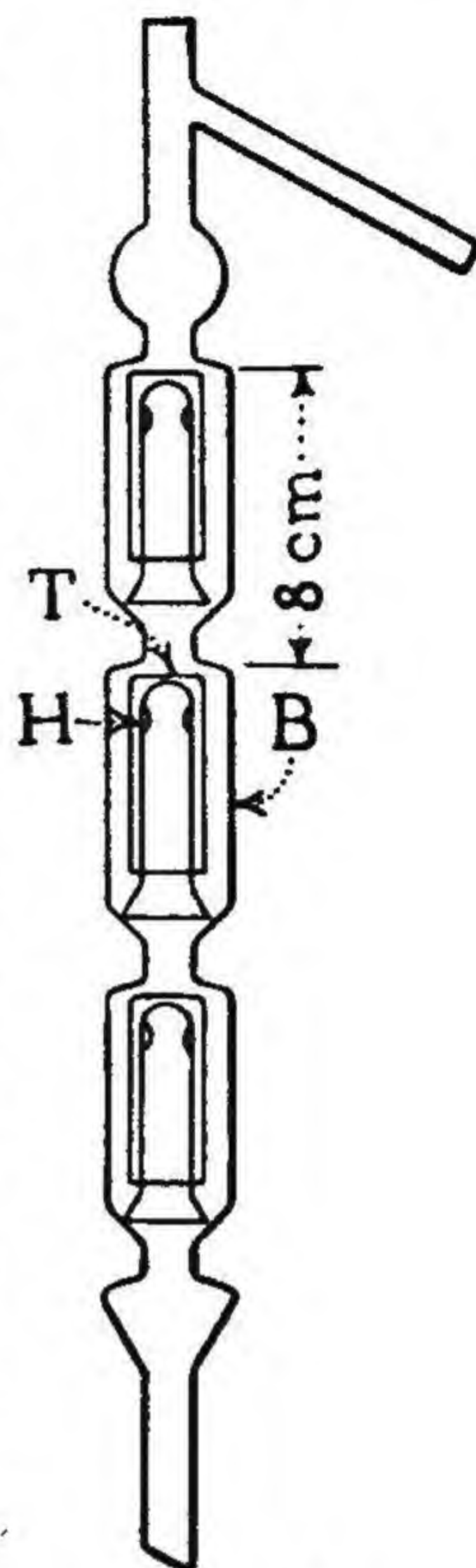


FIG. 38

yield a graph like A in Fig. 39. The thermometer would be placed, of course, at the top of the still-head near the opening to the condenser. The thermometer reading would remain perfectly constant at the boiling point of benzene, or any other more volatile constituent, until all of the benzene passes into the condenser. Then the temperature would rise at once to the boiling point of toluene, or any other



B would be obtained; and still-heads of intermediate efficiencies would give curves lying somewhere in between A and B.

Since it is in general difficult to operate different still-heads at the same rate, it would be better to plot boiling points against volume of distillate, rather than against time.

**Experiment.** Test the efficiency of several different types of still-head, using an approximately 50-50 mol mixture of benzene and toluene. Run a rapid stream of cold water through the condenser, and catch the distillate in a burette or graduate cylinder. A thermometer reading to  $0.1^{\circ}$ , and well shielded from draughts, should be used. Plot the results as indicated above.

An ordinary fractionating flask with an extra long still-head should be studied first; and then its column may be packed, first with pieces of broken glass tubing about 1 cm. long and 4-5 mm. diameter, and second with crystals of carborundum, of about the same size as the glass tubes, with plenty of sharp corners and edges. Also run a Young evaporator type still-head, described above.

If desired, the student may study various other types that may be available, to get an idea of relative efficiencies; e.g. such still-heads as the Rod and Disk type, the Linnemann, Glinsky, and Le Bel-Henninger, etc.

**REFERENCES:**

- Taylor, Chap. X.
- Rodebush, Chap. VII.
- Getman and Daniels, Chap. VII.
- Millard, Chap. V.
- Findlay, Chap. XIX.
- Eucken, Jette and LaMer.



## EXPERIMENT 17

### RECIPROCAL SOLUBILITY; COMPLETELY CLOSED SOLUBILITY CURVE

Only about a half-dozen liquid-liquid systems are at present known, the mutual solubilities of which vary with temperature in such a manner as to yield a completely closed solubility curve, such as the nicotine-water system; although it is possible that a great many liquid-liquid systems would be of this type if physical properties such as melting point and boiling point would permit. Recently, Cox and Cretcher of the Mellon Institute have reported (*J. Am. Chem. Soc.*, 48, 451 (1926)) interesting liquid pairs of this sort, consisting of water and the alkyl ethers of ethylene glycol, which are well adapted for laboratory experimentation.

#### EXPERIMENTAL

Mono-*n*-butyl ether of ethylene glycol\* is distilled and a fraction boiling within a few tenths of a degree is collected. This material and freshly boiled distilled water are then weighed into six glass tubes, each of about 15–20 cc. capacity and of the form shown in Fig. 40, as follows:

Tube 1.	1.00 g. glycol ether	9.00 g. water
Tube 2.	2.00                   “	8.00                   “
Tube 3.	3.00                   “	7.00                   “
Tube 4.	4.00                   “	6.00                   “
Tube 5.	5.00                   “	5.00                   “
Tube 6.	5.75                   “	4.25                   “

The contents of each tube weigh 10.00 g. The quantities may vary as much as 0.1 g. from those given but the weights of each liquid should be known to within 0.01 g.

The tubes may be conveniently made from well-formed and thick-walled test tubes. Tubes made from pyrex glass, however,

\* May be purchased from The Carbide and Carbon Chemical Corporation, 42nd St. and 5th Ave., New York City.



are much to be preferred. Since in the tubes, when they are heated, a pressure somewhat above atmospheric is generated, it is recommended that the instructor himself make up the tubes for this experiment so that he will be confident that no accident due to faulty tubes or to faulty sealing can occur. Such a set, once made, can be used over and over again by students.

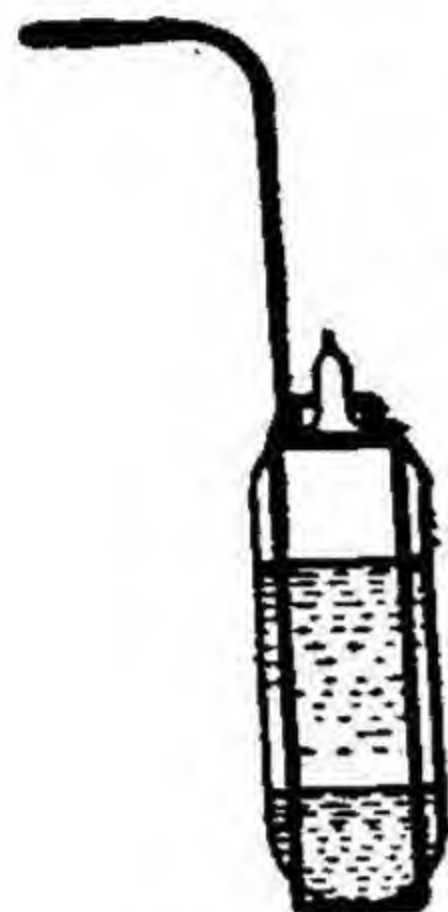


FIG. 40

After the tubes are supplied with the above mixtures, they are sealed off and the composition of their contents etched on the glass with hydrofluoric acid. To do this, coat the tube with a thin layer of melted paraffin and with a sharp point scratch through to the glass. Then with a small camel's hair brush or with a tuft of absorbent cotton fastened on the end of a match-stick or a file apply a little hydrofluoric acid.

Let the action of the acid continue for a minute or two, occasionally passing the brush over the figures so as to keep the grooves supplied with the acid. Then carefully wash off the excess acid and remove the paraffin by warming and wiping with a waste piece of cloth. (*Great precautions should be observed in handling hydrofluoric acid, as it burns the skin very seriously and painfully. The fumes should not be inhaled.*)

The six tubes are placed in a row in a wire holder, attachable to a motor-driven mechanical shaker operating vertically. The wire holder is made of spring brass wire; coils of spring brass at the bottom keep the tubes firmly in place. The mechanical shaker is provided so that the student will not be exposed to the danger of shaking the holder and tubes by hand; and the six tubes are mounted and shaken simultaneously so that the student will not have to handle any of the tubes while they are hot.

The bath in which the tubes are shaken consists of a three-liter pyrex beaker almost filled with mineral oil. It is gradually heated by means of a Bunsen burner, the temperature being indicated by a thermometer graduated in degrees. The temperature at which two liquid phases appear, is noted. This temperature, for each tube, should be approached from above, by cooling, as well as from below, and the two values should check within  $0.5^{\circ}$ – $1.0^{\circ}$ . It is advisable to determine it roughly first, with rapid heating, and then to redetermine it more carefully with slow heating.



The heating is now continued until the turbidity disappears at a higher temperature and each mixture in turn becomes homogeneous again. Again locate this temperature for each tube from above as well as from below.

*Precautions must be taken against accidents. Do not use a ring to support the heavy beaker of hot glycerine; a number of serious accidents caused by the breaking of such rings have recently been brought to our attention; always use a tripod and a wire gauze. Do not allow any water or other liquid to fall into the hot glycerine bath, as the sudden conversion of water into vapor may give a violent explosion. For this reason, also, the tubes used in the experiment should be without imperfections. Do not, under any circumstances, heat the bath to a temperature higher than  $135^{\circ}\text{C}$ . This precaution is necessary because the opalescence which persists near the consolute temperatures may lead students to heat the bulbs to a dangerously high temperature. The difficulty due to opalescence may be avoided by placing an electric light behind the bath, so that the contents of each tube may be viewed by transmitted light; the sharpness with which the wires of the holder may be seen through the mixtures provides a good criterion of their homogeneity. The experiment should be performed in a closed hood or behind a thick glass partition.*

As glycerine readily absorbs moisture from the air, it should be kept in a glass stoppered bottle when not in use. Before attempting to pour it back into the bottle, however, it should be allowed to cool to room temperature. Neglect of this precaution may lead to severe burns.

When the upper and lower temperatures have been determined for each mixture, plot these temperatures against the per cent of glycol-ether. What are the upper and lower consolute temperatures for this system? If a line be drawn connecting these two points, is the closed curve completely symmetrical about it as an axis? What is the physical significance of symmetry or departure from symmetry in such a curve? Draw the "tie-line" at  $100^{\circ}$ . If 20 g. of the glycol-ether and 30 g. of water were heated together to  $100^{\circ}$ , what would be the weight of each layer? Apply the phase rule to this system and indicate the number of degrees of freedom to be found in the various regions of the diagram.



# **ELEMENTARY PHYSICAL CHEMISTRY**

## **REFERENCES:**

**Taylor, Chap. X.**

**Rodebush, Chap. VII.**

**Getman and Daniels, Chap. VII.**

**Millard, Chap. IX.**

**Findlay, Chap. XIX.**



## EXPERIMENT 18

### MOLECULAR WEIGHT BY BOILING POINT ELEVATION

When a non-volatile solute is dissolved in a solvent, the vapor pressure of the solvent is lowered, and hence the boiling point of the solvent is raised. The ability of a solute to elevate the boiling point is a so-called *colligative* property, i.e. it does not depend on the *nature* of the solute molecules but only on the *number* of solute molecules dissolved in unit volume or unit mass of solvent; i.e., it depends on concentration. Freezing point depression, osmotic pressure, and relative lowering of vapor pressure also depend on the *number* of solute molecules and not on their chemical nature. Such a principle may be employed in the experimental determination of molecular weights of solute molecules, since it furnishes a method for virtually counting molecules, or at least a criterion for telling whether or not there are the same number of dissolved molecules in one sample of solvent as in another similar sample of the same solvent. If the numbers of solute molecules are the same in the two cases, regardless of whether they are the same *kind* of molecule, the boiling point elevations will be the same for the two solutions.

The development of this method for molecular weight determination starts with an arbitrary definition of a *molal boiling point elevation*, which is taken as the boiling point elevation which results when 1 mol (i.e.,  $6.06 \times 10^{23}$  actual molecules) of non-volatile, non-dissociating and non-associating solute is dissolved in 1000 g. of solvent. This molal elevation is represented by the symbol  $K_b$ . It differs for different solvents. It may be evaluated for a given solvent by experimental determination, and it can be calculated by proportion even if the particular solute chosen for the experiment is not sufficiently soluble to give a 1 molal solution (1000 g. solvent). Indeed  $K_b$  must be evaluated by working with a dilute solution and making the calculation by proportion, rather than with such a concentrated solution as 1 molal, because of the usual breaking down of simple functional relationships in concentrated solution.



$K_b$  may also be calculated approximately from the thermodynamically derived equation

$$\Delta T_b = \frac{RT^2}{\Delta H_v} \cdot N_B \quad (1)$$

where  $R$  is the gas constant,  $T$  the absolute temperature of the boiling point of the pure solvent,  $\Delta H_v$  the molar heat of *vaporization* of the solvent, and  $N_B$  the mol fraction of the solute. When  $N_B$  is such that 1 mol of solute is dissolved in 1000 g. of solvent, then  $\Delta T_b = K_b$ . (For a derivation of this equation, see Rodebush, pp. 155-9; or Getman and Daniels, pp. 167-70.) For example, in the case of water as solvent

$$K_b = \frac{1.99 \times (373)^2}{539 \times 18} \cdot \frac{1 \text{ mol}}{\frac{1000 \text{ g.}}{18 \text{ g.}}} = 0.514$$

as compared with the experimentally determined value of 0.512.

Once  $K_b$  for a solvent is evaluated, either experimentally or by calculation with Equation 1, above, molecular weight determinations of solutes dissolved in this solvent can be made. If  $\Delta T_b$  is the observed boiling point elevation when  $g$  grams of solute are dissolved in  $G$  grams of solvent, then

$$\frac{g}{G} : \Delta T_b = \frac{M}{1000} : K_b \quad \text{or} \quad M = \frac{1000 \cdot g \cdot K_b}{G \cdot \Delta T_b} \quad (2)$$

where  $M$  is the molecular weight of the solute molecules.

If any considerable degree of accuracy is to be obtained in measuring small differences of temperature, such as those encountered in boiling point elevation determinations, it is necessary to have available a very sensitive thermometer. Both the electric resistance thermometer and the multiple thermocouple meet this requirement admirably, but for the present purpose the Beckmann mercury thermometer serves well enough.

### THE BECKMANN THERMOMETER

The Beckmann thermometer, illustrated at T in Fig. 41, is made with a large bulb, so that a small rise of temperature will force a comparatively large volume of mercury up into the small capillary stem, and hence move the top of the mercury thread a con-



siderable distance along the scale. The Beckmann scale is marked in intervals of  $0.01^{\circ}$ , and with a magnifying glass it can easily be read to  $0.001^{\circ}$ . Such a thermometer necessarily covers only a small temperature range ( $5^{\circ}$ – $6^{\circ}$  on the Beckmann scale); otherwise the stem would be inconveniently long. But it is possible to work over a large temperature range through the provision of a reservoir of mercury R at the top of the thermometer. The thermometer must be "set" so that the desired temperature will be indicated on the scale. Suppose that we wish, as is the case in the present experiment, to determine the boiling point of acetone solutions. Acetone boils at about  $56.5^{\circ}$ . The thermometer bulb is immersed in a beaker of water which is gradually heated to a temperature of about  $62^{\circ}$  (several degrees above the desired temperature), as indicated by an ordinary mercury thermometer also in the water-bath. If there happens to be too much mercury in the bulb, it will be driven up the scale into the reservoir at the top. A gentle blow struck on the top of the thermometer with the hand will cause the capillary thread of mercury to break away from that in the reservoir, and when the bulb is cooled somewhat, the thread will descend on to the scale. If there is not enough mercury in the bulb to register on the scale, it must be warmed up until the thread reaches the reservoir. Then by inverting the thermometer and tapping gently, the extra supply of mercury in the reservoir and the thread are brought into contact, so that they cohere. Now, if the bulb is cooled, mercury is drawn over from the reservoir. In this way the required adjustments are made to bring the top

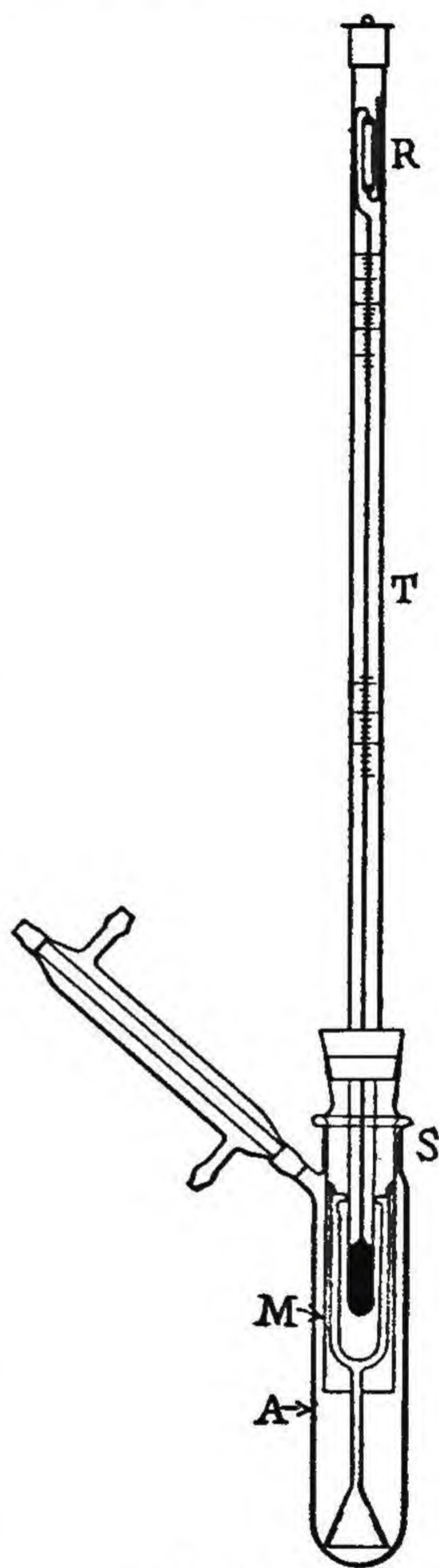


FIG. 41



of the mercury thread near the bottom of the scale for the boiling point of acetone. (Similarly, for freezing point lowerings, the mercury should be adjusted to be toward the top of the scale, when the bulb is at the temperature of the melting solvent.) Great care should be exercised in handling the thermometer, as it is quite fragile (and a Beckmann thermometer costs \$15-\$20).

The boiling points of pure liquids are easily and accurately measurable by virtue of the possibility of placing the thermometer bulb in the vapor phase. The condensing vapor forms a thin film of liquid on the bulb and this promotes a rapid attainment of equilibrium between the vapor and liquid phases. In the case of a boiling solution, however, since the temperature at which the vapor condenses on a thermometer bulb placed in the vapor phase is the same as for the pure solvent, the thermometer bulb must be brought in contact with the solution. The usual practice has been to immerse the thermometer bulb in the boiling solution, but in doing this, the thermometer is exposed to almost certain superheating, even with the most careful control of the heating, whether it be by gas flame or electrical. Furthermore, the boiling point of a liquid several centimeters below the surface may be as much as  $0.1^{\circ}$  too high, due to the effect of the hydrostatic pressure. Thus a large thermometer bulb, such as the Beckmann, gives merely a rough average of the temperatures existing throughout a considerable depth of liquid. To avoid mainly these two difficulties of superheating and of hydrostatic pressure, Cottrell has devised a novel form of the boiling point apparatus (*J. Am. Chem. Soc.*, **41**, 721 (1919)); the apparatus has been improved by Washburn, *J. Am. Chem. Soc.*, **41**, 729 (1919)).

#### THE COTTRELL BOILING POINT APPARATUS

The form of the apparatus is shown in Fig. 41. It consists essentially of a tube A containing the solution and provided with a side arm condenser, and with a ground glass stopper S which carries a cork stopper holding the Beckmann thermometer. Attached to the glass stopper are also two small glass delivery tubes of 1.5-2 mm. internal diameter, provided at their upper ends with jets, and joined to a vertical stem terminating at the bottom in a small funnel. When a few pieces of porous plate are added to prevent bumping, and the solution is carefully heated to boiling,



the bubbles of vapor which are produced rise into the funnel and, as they ascend the vertical stem, carry along small slugs of the boiling liquid. The solution is then squirted from the delivery tubes on to the thermometer bulb, whence it drips back into the bottom. The thermometer bulb is thus kept covered with a thin film of solution. Even if the boiling solution is somewhat superheated, the small portions delivered to the thermometer bulb will have ample time to come to thermal equilibrium with the vapor phase. Both the solution and the vapor in contact with it near the thermometer bulb are also under the same pressure. The thermometer is protected by the cylindrical glass shield M (which is an extension of the glass stopper) from being cooled by the drippings returning from the reflux condenser. It is important that this condenser be long enough to prevent any material escape of vapor from the tube. The funnel at the end of the "pump" should not be too small, else difficulty may be experienced in getting the pump to work; also the funnel should not be too flat. If pumping starts with difficulty, it is often possible to help matters by using a greater quantity of solvent, thus increasing the hydrostatic pressure at the funnel. The mouth of the funnel should be not far from the bottom of the container tube. J. R. Spencer, *J. Am. Chem. Soc.*, **43**, 301 (1921), describes a slightly modified, more rugged, form of the Cottrell apparatus.

#### EXPERIMENTAL

After having set the Beckmann thermometer for the boiling point of acetone, and with a stream of *cold* water flowing through the condenser, introduce a known weight of acetone (about 20 g.) into the tube, along with a few small pieces of clean porous plate. It is essential that the apparatus be protected from drafts of air, and that the heating be regular. Use a small gas flame from a micro-burner. After having once adjusted the flame to give a steady evolution of vapor, do not change it during the remainder of the determination. In order to start the pumping it may sometimes be necessary to shake the tube, or to lift out the glass stopper and its funnel attachment from the liquid and then replace it. While determining the boiling point, the Beckmann thermometer should be tapped every few seconds to prevent the mercury thread from sticking to the walls of the stem capillary. The tapping



may be done with a light wooden rod, such as a pencil, or better by a mechanically operated tapper.

After the temperature has become constant and the boiling point of acetone has been noted, add enough benzoic acid to make an approximately 2 per cent solution, and determine the rise in the boiling point. The benzoic acid should be compressed into little pellets either in a pellet machine or by forcing it into a small glass tube with a glass rod which just fits the tube, like a piston. If the pellets stick to the glass tube, they may be readily removed after warming the tube over a small flame. The pellets may be introduced into the acetone through the condenser. Determine also the boiling points of 4 per cent and 6 per cent solutions. From your results calculate the boiling point elevation,  $K_b$ , and from it the heat of vaporization of acetone. Compare your values with those given in tables of physical constants.

Determine the boiling point of a 4-5 per cent solution of  $\alpha$ -naphthol in acetone, and using your own value for the molar boiling point constant of acetone, calculate the molecular weight of  $\alpha$ -naphthol.

In this experiment it is necessary to know the weights of both solute and solvent fairly accurately, say to three or four significant figures. To weigh the solvent to a hundredth of a gram would necessitate weighing the apparatus as well, which would be cumbersome. From a manipulative point of view it would be easier to use a definite volume of solvent in each determination. By weighing this volume (delivered from a pipette) of solvent once, in a beaker or flask, the same volume could be used in succeeding determinations without any further weighing, by using the same pipette at the same temperature each time.

Probably the largest error in the determination of molecular weights by this method arises from the loss of solvent by evaporation through the ground glass joint, and the condenser. By drawing off samples of the solution for analysis at the time of the thermometer reading, very precise results may be obtained, but the student is not asked to carry out this operation in the present experiment. It should be remembered, too, that the boiling point may change *during* the determination because of a change in atmospheric pressure. One way of eliminating such a possible error is to employ two sets of the Cottrell apparatus



simultaneously, one with the solution and the other with pure solvent.

Various other solvents, other than acetone, may be used in this experiment, as well as other solutes, as the instructor or student may desire. The values of  $K_b$  for some common solvents are given in the following table.

TABLE X  
VALUES OF  $K_b$

Solvent	B.p. at 760 mm.	$K_b$	Correction in B.p. per 10 mm.
Water.....	100°	0.512	0.08
Benzene.....	80.3	2.43	.24
Carbon disulfide.	46.3	2.24	.20
Chloroform.....	61.2	3.41	.10
Ethyl alcohol....	78.5	1.14	.10
Ethyl ether.....	34.5	2.01	.07
Ethyl acetate....	77.1	2.52	.12

A useful micro boiling point method has been developed by Pregl. One is able to work with such small quantities as 3 milligrams of solute in 1.5 cc. of solvent. (*Quantitative Organic Micro-analysis*, by Pregl, 1924, translated by Fyleman, cf. Barger, *Ber.*, 54, 1979; 55, 1051 (1921).)

REFERENCES:

- Taylor, Chap. VIII.
- Rodebush, Chap. VII.
- Getman and Daniels, Chap. VIII.
- Millard, Chap. V.
- Findlay, Chap. VIII.



## EXPERIMENT 19

### APPARENT MOLECULAR WEIGHT OF POTASSIUM CHLORIDE; FREEZING POINT METHOD

#### EXPERIMENTAL

In the present method for determining the lowering of the freezing point of the solvent produced by a solute, satisfactory measurements can be made with a thermometer graduated to  $0.1^{\circ}$ , on which the temperature can be estimated to  $0.01^{\circ}$ , but it is more desirable to make use of a Beckmann thermometer. This should be adjusted so that the freezing point of water is near the top of the scale (directions for setting the Beckmann thermometer are given in Exp. 18). A Dewar test tube, or a thermos bottle, of about 400–500 cc. capacity is provided with a cork stopper through which the thermometer is inserted, so that the thermometer bulb extends to about 2 cm. from the bottom. The cork also has a hole to permit the insertion of a 10 cc. pipette, which is provided at its lower tip with a filter made of a short piece of rubber tubing stuffed with a loose wad of absorbent cotton.

Clean the thermos bottle and fill it about half full of finely crushed clean ice. In selecting the ice, the clear ice on the outside of the block is preferable as it contains less dissolved material. Add enough distilled water to permit easy shaking of ice and water. With the thermometer in place shake the bottle and record the temperature every half minute. To get uniform results this shaking should be kept up at a constant, steady rate and the thermometer should be tapped lightly to prevent the mercury from sticking. Continue taking the temperature readings until about ten have been secured which vary not more than  $0.01^{\circ}$  from one another. The average of these readings is taken as the freezing point of water.

Prepare a solution of about 20 g. of pure potassium chloride in 100 cc. distilled water. Keeping the thermometer inside the thermos bottle as much as possible, drain out the water and substitute the salt solution, adding more if necessary. Insert the



pipette (with filter attached) and, shaking the bottle at the same rate as before, again take temperature readings every half minute. At first the temperature will fall, then it will be fairly constant for a number of readings and finally will begin to rise again. The solution should be concentrated enough so that the reading is near the lower end of the thermometer scale. When it is noted that the temperature is rising at a constant rate, withdraw 3 or 4 cc. of the solution by means of the pipette, and run it into a small weighed Erlenmeyer flask. With the more dilute solutions correspondingly larger amounts should be withdrawn. Determine the weight of the sample and titrate it with a standard 0.1 *N* solution of silver nitrate, using sodium chromate as indicator. From these data the weight of the salt and the weight of the water are calculated.

The student should himself standardize the silver nitrate solution against known weights of potassium chloride. This procedure will give him frequently much-needed experience in titrating and will help him to get consistent end-points.

The temperature on the Beckmann thermometer must be noted at the instant of the withdrawal of the sample of solution, since the temperature is steadily changing; or the time of withdrawal may be noted and the corresponding temperature read from a plot of temperature against time.

Add enough water to the contents of the thermos bottle, and more ice if necessary, to raise the freezing point about 0.5°, and again determine the freezing point lowering and the weights of solvent and salt. Repeat this procedure until finally the solution contains less than 1 per cent potassium chloride. In case the series is interrupted so that the thermometer comes to room temperature, it is advisable to redetermine the freezing point of pure water.

Calculate the apparent molecular weight of potassium chloride at the various concentrations, by using the following equation (similar to Equation 2, Exp. 18),

$$M = \frac{1000 \cdot g \cdot K_f}{G \cdot \Delta T_f}$$

where *M* is the molecular weight, *g* and *G* the weight in grams of solute and solvent respectively,  $\Delta T_f$  the observed freezing point depression, and *K<sub>f</sub>* the molal freezing point depression



(for water,  $K_f = 1.858$ ). As in the case of  $K_b$  (see Exp. 18),  $K_f$  for any solvent may be calculated, but in this case from  $\Delta H_f$ , the molar heat of fusion, by means of the equation

$$K_f = \frac{RT^2}{\Delta H_f} \cdot \frac{1 \text{ mol solute}}{1000 \text{ g. solvent}}.$$

The degree of ionization  $\alpha$  may be calculated for weak electrolytes by means of the equation

$$\alpha = \frac{i - 1}{n - 1}$$

where  $n$  represents the number of ions yielded by dissociation of one molecule ( $n$  for KCl is 2), and where  $i$  is the van't Hoff factor,  $\left(\frac{\Delta T_f}{\Delta T_f}_0\right)$ , namely the ratio of the actually observed freezing point depression to the depression which would have been observed if the solute were not dissociated at all into ions. In the case of strong electrolytes, like KCl,  $\alpha$  has a doubtful meaning. The concept of activity coefficient is much more useful, but a discussion of activity and activity coefficient, and a description of methods for evaluating them from freezing point data, are beyond the scope of this manual. The student should consult Getman and Daniels, pp. 510-22; and Lewis and Randall, pp. 341-63; or other references.

While water is perhaps most frequently employed as solvent in measurements of freezing point depression, there is no reason why other convenient solvents, for example various organic solvents, should not be used. A successful micro method has been developed, involving the use of only very small amounts of the organic solute, the molecular weight of which is to be determined. Solvents are chosen that have very large values for  $K_f$ , such as camphor ( $K_f = 49.80$ ), tribromophenol ( $K_f = 20.4$ ), etc., so that the observed  $\Delta T_f$  produced by the tiny amounts of solvent may be made large enough for convenient measurement. The values of  $K_f$  for some of the more commonly used solvents are given in the following table.



TABLE XI  
VALUES OF  $K_f$

Solvent	Freezing point	$K_f$
Water.....	0°	1.855°
Benzene.....	5.4	5.12
Camphor.....	179	49.80
Naphthalene.....	80	6.8
Nitrobenzene.....	5.7	7.0
Phenol.....	38.5	7.4
Tribromphenol.....	95	20.4

REFERENCES:

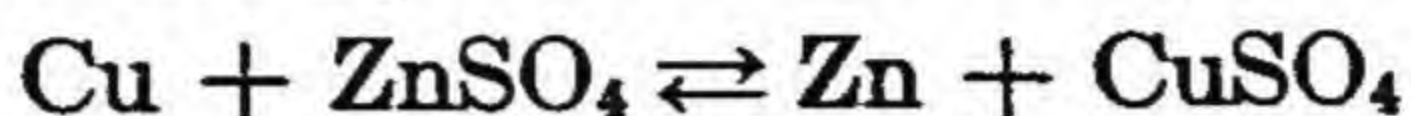
- Taylor, Chap. VIII.  
 Rodebush, Chap. VII.  
 Getman and Daniels, Chap. VIII.  
 Millard, Chap. V.  
 Findlay, Chap. VIII.



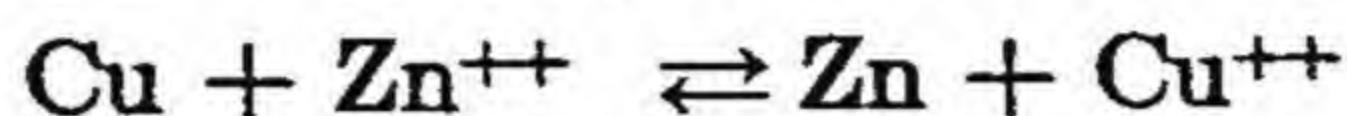
## EXPERIMENT 20

### CALORIMETER; HEAT OF REACTION

This experiment may be performed separately, for its own sake, or in conjunction with Exp. 35. The heat,  $\Delta H$ , of the reaction



or



is to be determined. This reaction is purposely selected for study in order that a comparison may be made between the calorimetrically measured heat and that predicted by the Gibbs-Helmholtz equation from the observed E.M.F. and temperature coefficient of the E.M.F. in a Daniell cell (Exp. 35). Such a comparison should help the student to appreciate the important and fundamental relationship between the thermal energy and free energy of a naturally occurring process.

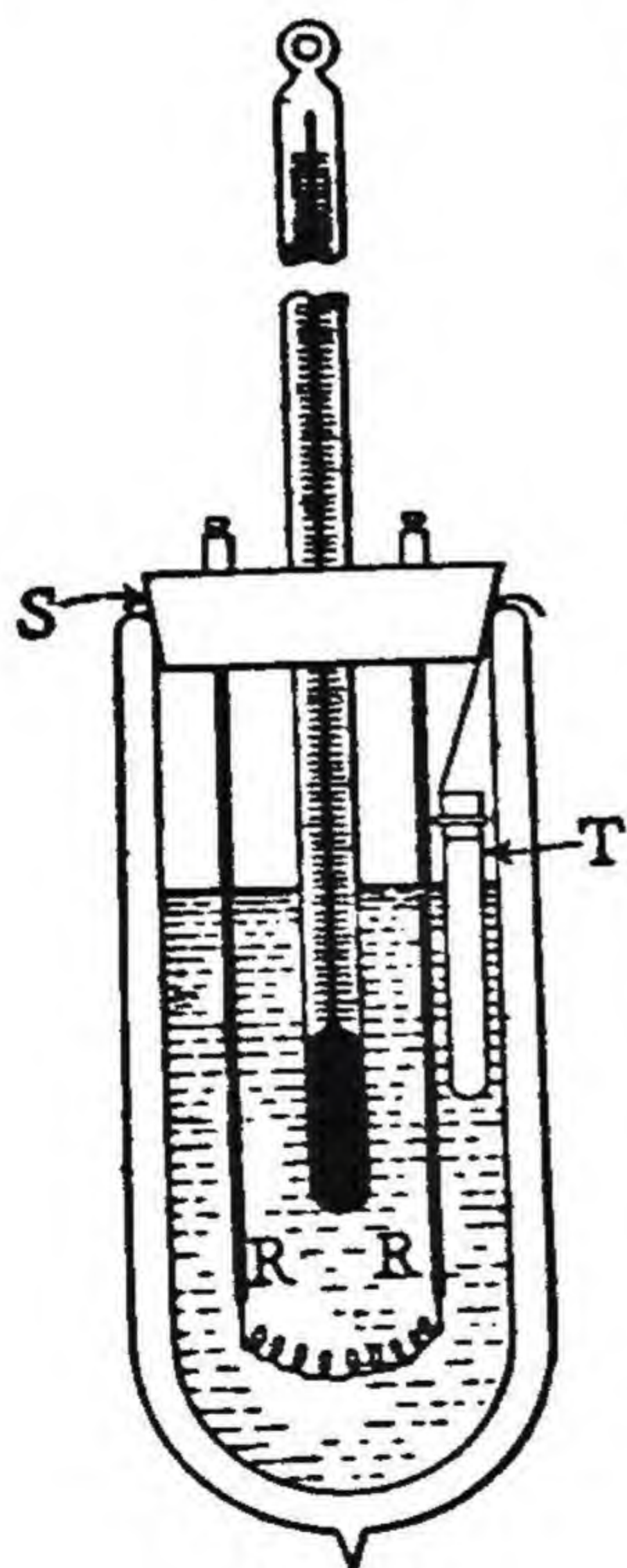


FIG. 42

**Directions.** The calorimeter vessel, consisting of a silvered Dewar test tube or a thermos bottle of about 400–500 cc. capacity, is shown in Fig. 42. The cork stopper S carries a thermometer having a range of about 10°–50°, and graduated in 0.1° intervals (a Beckmann thermometer is not needed), together with two brass rods RR equipped with binding posts and soldered or clamped at their lower ends to a small coil of about No. 22 B. & S. gage nichrome wire (or platinum or other resistance wire), long enough to have a resistance of 1–2 ohms. The Dewar tube should be further insulated by packing it in cotton in a glass jar or small wooden box.

A solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is prepared so as to contain 1 mol  $\text{CuSO}_4$  per 100 mols of water. A weighed quantity (about 100 g.) of this solution is placed in the Dewar tube at room temperature



and the exact temperature determined by placing the stopper carrying the thermometer in the Dewar tube and noting its reading. An excess of pure zinc dust, about 9 g., (which, after weighing in the test tube T, may or may not be hung inside the Dewar to come to the temperature of the  $\text{CuSO}_4$  solution) is then dumped into the solution and the stopper is quickly replaced. The flask and contents are then shaken with a swirling motion and the maximum temperature rise is observed. Care must be taken not to shake too violently, as this in itself will produce a slight temperature rise. When the maximum temperature (use reading glass) has been attained and recorded the flask and contents are then cooled to the initial temperature. The cooling may be hastened by circulating tap water through a U-shaped glass tube immersed in the Dewar tube. As soon as the initial temperature has been reached, a 6-volt storage battery, which should be in good condition and able to furnish a steady current, is connected to the binding posts RR, in series with an ammeter and an adjustable rheostat of small resistance. By this arrangement a constant heating current of 2–3 amperes is passed through the nichrome coil until the temperature has been raised from the initial value to the maximum value. The time required for this electrical heating is measured with a stop watch. The heat generated electrically in calorimeter is given by the equation

$$q = 0.239 \cdot i^2 \cdot r \cdot t \quad (1)$$

where  $q$  is expressed in calories,  $i$  in amperes,  $r$  in ohms and  $t$  in seconds. The resistance  $r$  of the nichrome coil may be determined while the heating current is flowing, by connecting the binding posts RR to a voltmeter (of high resistance) with a scale reading to 0.01 volt, and calculating the resistance from the known value of the current and the voltage drop through the coil.

The value for  $-\Delta H$ , the heat evolved per mol in this reaction is therefore given by the equation

$$-\Delta H = (0.0239 \cdot i^2 r t) \times \frac{\text{atomic weight of copper}}{\text{weight of copper precipitated}}$$

Enough zinc (9 g.) has been added to precipitate all of the copper.

Check determinations should be made and in general the values obtained should agree within 2% of each other.



The procedure followed in this experiment is readily adaptable to most reactions occurring in solution and possesses the advantage of automatically correcting for thermal leakage, for the heat capacity of the calorimeter and accessories, and for the specific heat of the solution, which is not exactly 1. In this connection it is advisable to have the time of electrical heating the same as that required for the maximum temperature rise to be attained.

**REFERENCES:**

- Taylor, Chap. II.
- Rodebush, Chap. V.
- Getman and Daniels, Chap. XI.
- Millard, Chap. VII.
- Findlay, Chap. X.
- Eucken, Jette and LaMer.



## EXPERIMENT 21

### THE BOMB CALORIMETER; HEAT OF COMBUSTION

The heat of combustion of a substance, defined as the heat liberated by the complete oxidation of one gram-molecule of that substance, may be determined experimentally by means of one of the numerous types of bomb calorimeters. It will be assumed that a Parr oxygen bomb calorimeter is available for the present experiment, but the general procedure outlined here may be carried through with other standard types of bomb calorimeters.

Figure 43 illustrates the apparatus. The bomb B is made of the alloy illium, to resist the solvent action of the acids generated during combustion, and to withstand considerable gaseous pressure. The bomb fits at O into an octagon shaped holder, and the lid L can be screwed down (a rubber gasket fits between the lid and bomb) with a spanner wrench. The lid is provided with an inlet and outlet valve V, kept closed automatically when the bomb is loaded with gas. To V are attached the pressure gage and connections leading to the oxygen tank. The two metal supports SS hold the nickel capsule C which contains the combustible substance, and also hold the piece of fine iron wire, which is heated

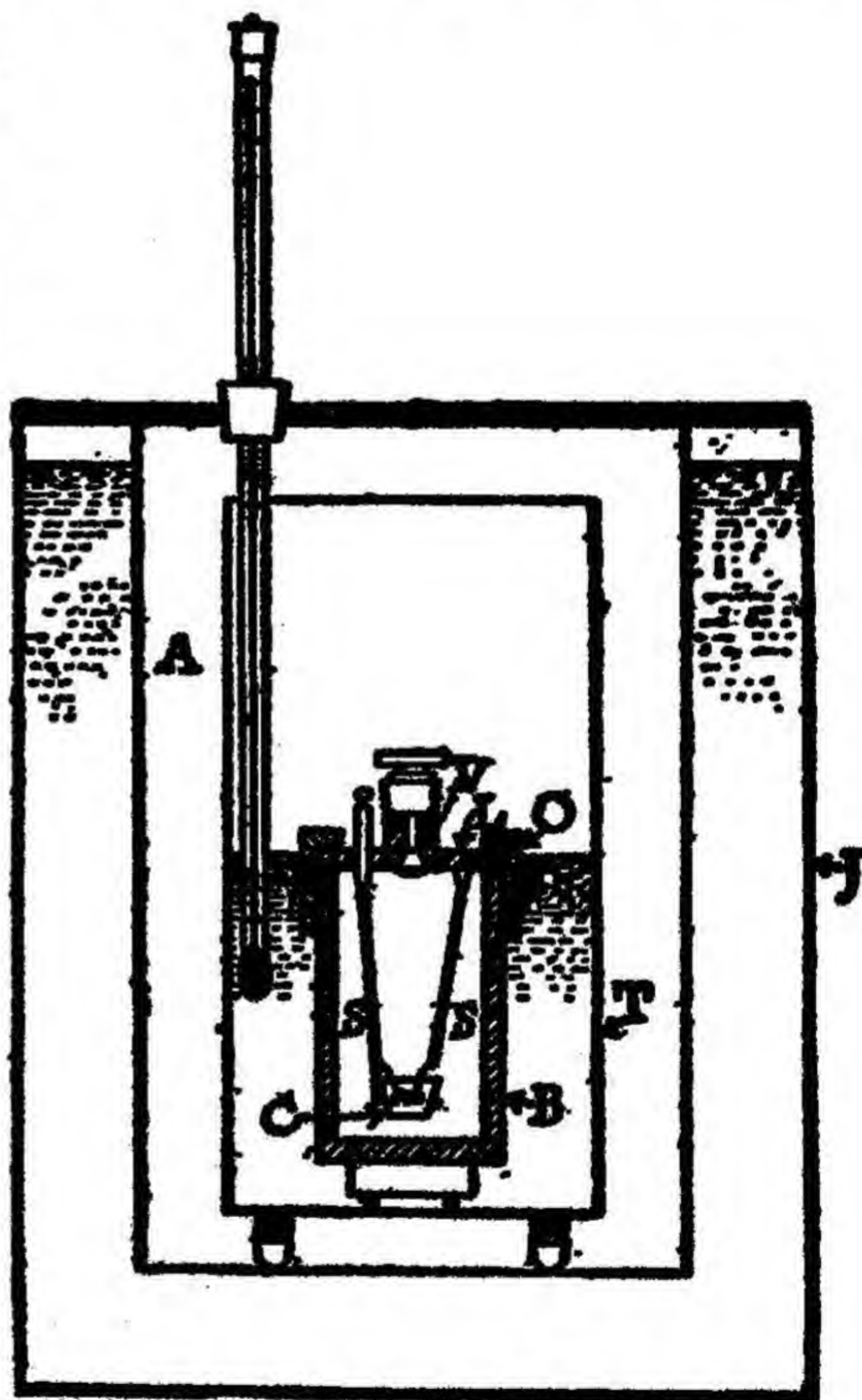


FIG. 43



electrically to ignite the charge. Only a short length of the wire is required, but its weight should be obtained so that its heat of oxidation may be subtracted from that generated by the main reaction. The necessary information regarding the heat of combustion of iron is generally supplied with the spool or card on which the wire is furnished, or it may be obtained by consulting tables of chemical constants. It is best to weigh a meter length of wire and then calculate the weight of the actual length used. This is not only more accurate, but it makes one weighing sufficient for all the determinations which the student is required to perform. The wire may be heated with a battery of about 12 volts, or if desired with the 110-volt electric light current. After the combustion, when the bomb is opened, any unburned portions of the wire should be collected and weighed and allowed for in making the correction.

In the capsule is placed a known weight (0.5–1.5) grams of the combustible substance, in the form of a *compressed pellet or tablet* with a portion of the iron wire imbedded in it; the wire may be imbedded by heating it momentarily in a flame and touching it to the pellet; this must be done, of course, before the pellet is weighed. The quantity of substance is chosen so that the temperature rise in the calorimeter will be about  $2^{\circ}$ . At least three times the quantity of oxygen gas needed for complete combustion is introduced into the bomb, and this generally means 20–25 atmospheres as measured on the pressure gage. The correction for the heat of oxidation of the nitrogen of the residual air in the bomb may be neglected in this experiment. After the bomb is filled with oxygen, it is disconnected from the gas line, and immersed in the calorimeter vessel T (Fig. 43), containing about 2000 cc. or more of water, enough to cover the bomb up to the point O. The weight of this water to within one gram should have been previously determined. The water is stirred, preferably automatically, during the determination (the stirring mechanism is not shown in Fig. 43), and the rise in temperature is observed with a Beckmann thermometer, supported with its bulb in the water. The outer jacket J is filled with water, which has been allowed to come to room temperature. A thermometer with  $0.1^{\circ}$  graduations is hung in the air space A, and the temperature of the water in T is adjusted to be about  $1^{\circ}$  lower than that of A, so that the temperature after the



combustion will be as much above the temperature of the air space A (about  $1^\circ$ ) as the initial temperature is below it, to compensate as far as possible for any error due to radiation.

When the bomb has been filled, sealed and placed in the water, the stirrer started and the thermometers placed in position, take temperature readings every minute for about 10 minutes, or until practically constant temperature adjustment has been reached. Then fire the charge, and again note the temperature on the Beckmann thermometer every half-minute while the temperature is rising, and then every minute for about 10 minutes. Plot temperature against time, and extrapolate the line AB, in Fig. 44, until it intersects the extension of line CD. Line AB represents the rate of temperature decrease, when this rate has become

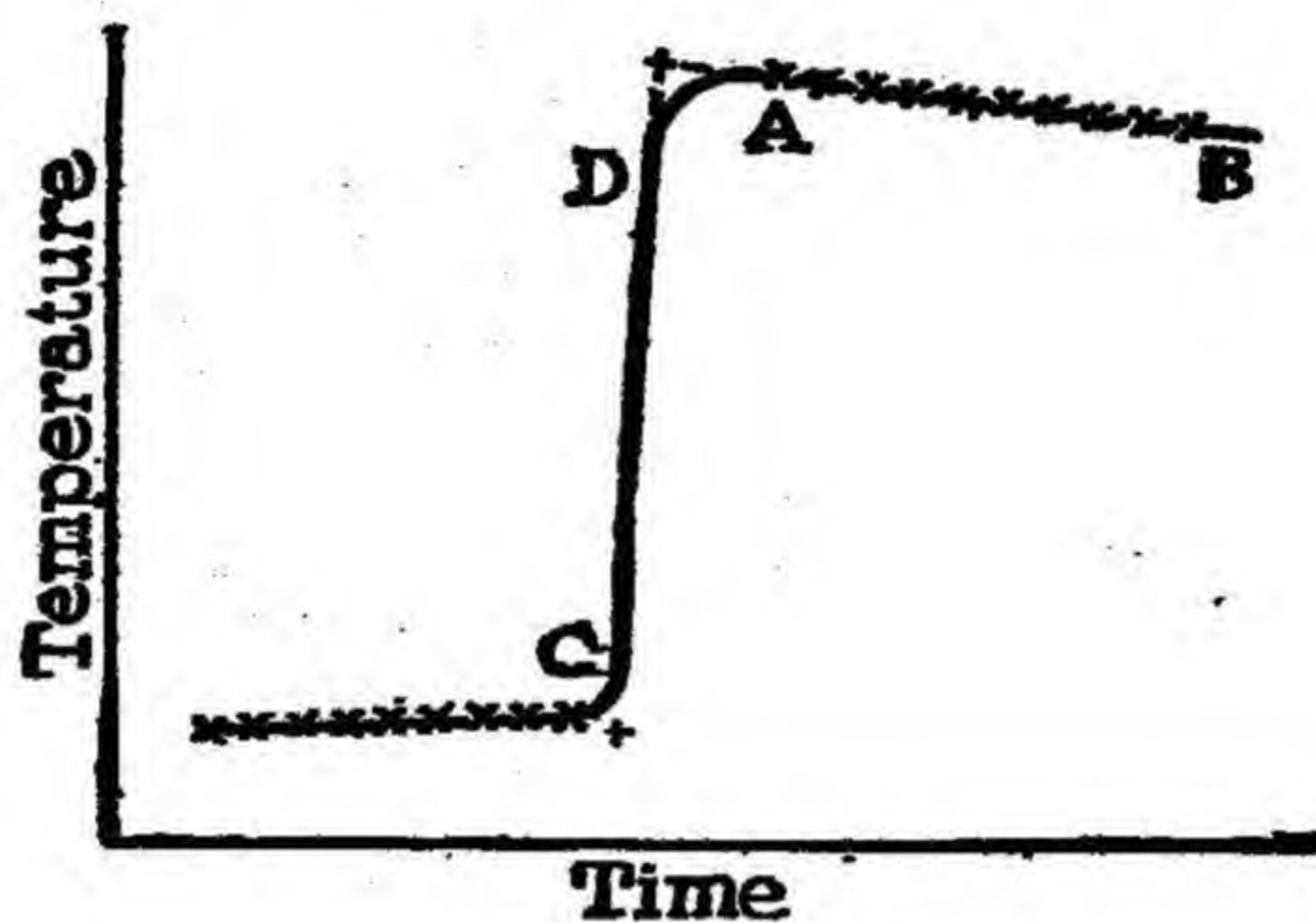


FIG. 44

practically constant, and the intersection of AB with CD gives the highest temperature which would have been attained as a result of the combustion, if there had been no losses due to thermal radiation. Such a graphical method of correction is frequently employed in calorimetric determinations.

Finally remove the bomb from the water, dry it and release the gas by pressing down the valve V. The lid may then be unscrewed with the spanner wrench.

The heat of combustion at constant volume,  $Q_v$ , may be calculated from the equation

$$Q_v = \frac{M}{m} (W + w)(t_1^\circ - t_2^\circ) \text{ calories}$$

where  $M$  is the molecular weight of the substance,  $m$  the weight



in grams oxidized in the bomb,  $W$  the weight of the water in the calorimeter,  $w$  the water equivalent of the calorimeter, and  $(t_1^\circ - t_2^\circ)$  the rise in temperature. When the temperature rises, the metal bomb and other parts of the calorimeter absorb some heat. By "water equivalent" is meant that quantity of water which will absorb just that amount of heat absorbed by the calorimeter parts, exclusive of the water in  $T$ . Instead of estimating the water equivalent from the mass and specific heat of the various calorimeter parts, or by generating a known amount of heat in the bomb with an electric current, and determining  $w$  from the observed temperature rise, as in Exp. 20, it is more convenient to oxidize a known weight of substance the heat of combustion of which is already accurately known.

Taking benzoic acid, about 0.5 gram, as the standard substance (heat of combustion,  $Q_v = 771,550 \pm 150$  calories) determine the water equivalent of the bomb calorimeter. Then determine the heat of combustion of camphor or naphthalene, repeating each determination as a check. Determinations in the bomb calorimeter give, of course, the heat of combustion at constant volume,  $Q_v$ . From your results calculate the heats of combustion at constant pressure,  $\Delta H$ .

#### REFERENCES:

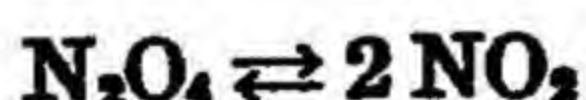
- Taylor, Chap. II.
- Rodebush, Chap. V.
- Getman and Daniels, Chap. XI.
- Millard, Chap. VII.
- Findlay, Chap. X.
- Eucken, Jette and LaMer.
- Richards and Davis, *J. Am. Chem. Soc.*, **42**, 1599 (1920).



## EXPERIMENT 22

### EQUILIBRIUM; DEGREE OF DISSOCIATION OF $\text{N}_2\text{O}_4$

In this experiment the *degree of dissociation* of  $\text{N}_2\text{O}_4$  will be determined



at a series of temperatures, and the *equilibrium constants*, and the *heat and free energy of dissociation* calculated. An easy and very successfully applicable technique for getting the degree of dissociation is the measurement of the gas density with the Dumas bulb. (See Exp. 1.)

Take a Dumas bulb (about 100 cc.), which is clean and dry on the inside, and provided with a capillary tube and stop-cock, as shown in Fig. 45. The stop-cock should be lubricated with a minimum amount of *vaseline*. Connect to an oil pump, or other pump capable of producing a vacuum as good as 1 or 2 mm. pressure, and evacuate. Wipe the bulb carefully with a piece of clean dry absorbent cloth, and weigh the evacuated bulb, to 0.1 mg. Then fill with dry air at atmospheric pressure, by opening the stop-cock and sucking in air through a  $\text{CaCl}_2$  drying tube. Weigh again. From the difference in weights in the two cases, and from the calculated density of dry air at the observed room temperature and atmospheric pressure, the volume of the bulb can be obtained with considerable accuracy. (1 liter dry air at N.T.P. weighs 1.293 g.) No correction for buoyancy of air need be made. Why?



Fig. 45

Obtain from the instructor a small sealed test tube containing about 5 cc. pure liquid  $\text{N}_2\text{O}_4$ ; or prepare some  $\text{N}_2\text{O}_4$  by thermally decomposing some  $\text{Pb}(\text{NO}_3)_2$  and condensing the vapors in a test tube immersed in an ice-bath; or prepare it by allowing 100 g.  $\text{HNO}_3$  to react with 50 g.  $\text{As}_2\text{O}_3$  in a 250 cc. flask, provided with a thistle tube for adding the  $\text{HNO}_3$ . The speed of the reaction may be regulated by heating or cooling the flask. The gases are lead



first through an empty glass bottle, to condense as much water as possible, and then into a large U-tube packed with beads or broken glass and immersed in a cold 3 : 1 ice: salt mixture. Here the  $\text{N}_2\text{O}_4$  condenses. Afterwards the cold  $\text{N}_2\text{O}_4$  should be purified by bubbling a slow stream of oxygen gas (from a tank) through it to remove  $\text{NO}$  and  $\text{N}_2\text{O}_3$ , until a pale amber color is obtained. Then the  $\text{N}_2\text{O}_4$  should be slowly distilled through a drying tube containing lumps of freshly heated calcium nitrate (since  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  react with most of the common drying agents), and finally condensed in a cold U-tube.

Cool 5 cc. of the  $\text{N}_2\text{O}_4$  liquid in a small test tube in an ice-bath, and having again evacuated the Dumas bulb and closed the stop-cock, thrust the end of the capillary into the  $\text{N}_2\text{O}_4$ , carefully open the stop-cock and thus slowly force about 4 cc. of the liquid  $\text{N}_2\text{O}_4$  up into the bulb without allowing any air to enter, except the air already in the capillary. This amount of air is negligibly small.

Now, immerse the bulb completely (to the junction with the capillary) in a large beaker of water, hand regulated to  $40^\circ\text{C}$ ., with the capillary held vertically above the water with a clamp. Let the bulb come to the temperature of the bath for about 5 minutes, open the stop-cock and after the liquid has completely disappeared off the bottom of the bulb and the brown gas no longer escapes from the upper open tip of the capillary, allow the bulb to remain for 1 minute longer. Then close the stop-cock, remove the bulb from the bath, dry carefully with the same piece of cloth used previously, and weigh again to 0.1 mg. Again immerse in a hot water-bath, but this time at  $50^\circ$ . Repeat the previous procedure. Repeat at  $60^\circ$ ,  $70^\circ$ ,  $80^\circ$  and  $90^\circ$ , using the original Dumas bulb throughout. In every case hold the temperature constant to  $0.1^\circ$ , if possible, and note the temperature on a reliable thermometer. The barometric reading (see Exercise II) should be taken also, of course, for every case.

Now all the data, needed for calculation of the degree of dissociation in the equilibrium mixtures of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$ , are available. First, calculate the density,  $d_2$ , in g./cc., of every mixture at the various temperatures. Then, assuming that these mixtures follow ideal gas behavior, two procedures are possible in calculating  $\alpha$ , the degree of dissociation: Taking the molecular weight of  $\text{N}_2\text{O}_4$



as 92.02, either the density  $d_1$  of the undissociated  $\text{N}_2\text{O}_4$  may be calculated for the various temperatures and barometer readings; or the density  $d_2$  of the various equilibrium mixtures may be calculated to N.T.P. In either case, the degree of dissociation can then be calculated from the equation,

$$\alpha = \frac{d_1 - d_2}{d_2(n - 1)}$$

where  $n$  is the number of molecules formed by the dissociation of one parent molecule, namely 2 in the present case of  $\text{N}_2\text{O}_4$ . Make up a table, listing temperatures,  $40^\circ$ ,  $50^\circ$ ,  $60^\circ$ , etc., in the first column, and the respective degrees of dissociation,  $\alpha$ , in the second column. In the third column list the respective values of  $K$ , the equilibrium constant, for every temperature, calculated from the equation (see Rodebush, pp. 83-85).

$$K = \frac{4\alpha^2 \cdot P}{1 - \alpha}$$

where  $P$ , the pressure, is expressed in *atmospheres*.

Now, take the following equation, which gives the variation of  $K$  with temperature,

$$\frac{d \ln K}{dt} = \frac{\Delta H}{RT^2}$$

where  $\Delta H$  is the heat of dissociation per mol, and integrate it, (1) first, without limits, and (2) second, between limits. Taking (1), plot  $\log K$  at  $40^\circ$ ,  $50^\circ$ ,  $60^\circ$ , etc., against  $\frac{1}{T}$  and determine the value of  $\Delta H$  graphically, from the slope. Taking (2), substitute values of  $K$  (from the third column of your table)  $10^\circ$  apart, and calculate values of  $\Delta H$ . Enter these values in a fourth column. How does the average of these  $\Delta H$  values compare with  $\Delta H$  determined graphically?

Finally, calculate the value of the equilibrium constant  $K_{25}$  at  $25^\circ \text{C}$ ., and assuming that the perfect gas laws hold, calculate the standard free energy  $\Delta F^\circ$  of the reaction  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  at  $25^\circ$ , from the equation,

$$\Delta F^\circ = -RT \ln K_{25}^\circ.$$



Surprisingly satisfactory values for  $\alpha$ ,  $K$ ,  $\Delta H$  and  $\Delta F$  can be obtained by carefully following the experimental technique given above, if a good pure sample of  $\text{N}_2\text{O}_4$  is employed.

Let the student attempt to derive the equation  $\frac{d \ln K}{dt} = \frac{\Delta H}{RT^2}$  by a Boltzmann factor treatment. (See Exercise III and Exp. 8.)

REFERENCES:

- Taylor, Chap. IX.
- Rodebush, Chap. V.
- Getman and Daniels, Chap. XII.
- Millard, Chap. VIII.
- Findlay, Chap. XI.
- Eucken, Jette and LaMer.



## EXPERIMENT 23

### BISMUTH-CADMIUM COMPOSITION MELTING- POINT DIAGRAM; THERMOCOUPLE; PHASE RULE

#### EXPERIMENTAL

Make four alloys of bismuth and cadmium containing 20, 40, 60 and 80 per cent of bismuth, the total weight of each sample being 100 g., by melting the proper amounts in a hard glass or pyrex test tube surrounded by sand in a large iron crucible (about 300 cc.). Using a thermocouple (see below) with a millivoltmeter, read the electromotive force every half minute as these molten alloys are allowed to cool *slowly*. Do the same with 100 g. samples of the pure metals. Use precautions against draughts of air during the cooling. To prevent oxidation keep a 5 to 10 mm. layer of ceresine wax over the metal.

Plot the electromotive force against the time of cooling for each sample and determine the electromotive force at the points where the slope of each curve undergoes a sudden change. An aid in doing this is to take two straight edges (e.g., two sheets of paper) lay one on each side of the point so that they coincide for a short distance with the plotted points and take their intersection as the point sought. At the other side of the graph, after having calibrated the thermocouple as described below, indicate the temperature of each such break in the curves. The curves for the pure metals and for the alloy containing 40 per cent cadmium will have only one break.

Now plot the temperature of the breaks so determined against the percentage composition of the alloys and draw smooth curves through the points. Draw also a straight horizontal line through the point of intersection of the two curves and a similar vertical line downward from the intersection. The curves and lines divide the graph paper into five sections, as indicated in Fig. 44.

#### THERMOCOUPLE

Over a century ago, Seebeck discovered that a small electric current flows through a circuit made of two different metals when the two junctions are at different temperatures. No difference



in the electromotive force exhibited is made by the introduction of a third metal, at any point in the circuit, provided that the two junctions of the new metal are at the same temperature.

Make a thermocouple by taking two lengths, about a meter long, of chromel wire and one of alumel (about No. 22 B. & S. gage) and joining one end of one chromel wire to one end of the alumel wire and one end of the other chromel wire to the other end of the alumel wire. The joining is most conveniently done by winding together the ends for a distance of 5 mm. and then fusing the extreme ends in a small oxygen-gas flame.

Slip a 15–20 cm. length of capillary glass tubing over each chromel wire to the junctions, for insulation, and attach the free ends of the chromel wire to a millivoltmeter having a scale reading from zero to ten millivolts. One junction is kept at a constant temperature by being immersed in crushed ice and the other junction is placed in a small glass vaccine tube, or a tube made from thin glass tubing about 10 or 15 cm. long, which is inserted into the molten bismuth-cadmium alloy. Each sample of metal should be provided with such a tube, which may be left imbedded in the solidified alloy; this obviates the necessity of reheating the metal to remove the tube and of dissolving off any adhering particles of alloy. It may be found necessary to use a clamp in order to keep the tube inserted to a sufficient depth in the molten alloy.

After having plotted the cooling curves for the two pure metals and for the alloys the thermocouple is to be calibrated by plotting millivolts against the known melting points of the two metals and their eutectic. These temperatures are, bismuth,  $271^{\circ}\text{C.}$ ; cadmium,  $321^{\circ}\text{C.}$ ; eutectic,  $149^{\circ}\text{C.}$  By drawing a smooth curve through these three points one is able to read off the temperature corresponding to any observed electromotive force.

When such a base-metal thermocouple is being employed extensively for the measurement of temperatures, frequent calibrations should be made, because the electromotive force of the thermocouple undergoes permanent changes, especially at high temperatures. For more accurate work a platinum-platinum rhodium thermocouple should be used, and the electromotive force be measured with a potentiometer instead of a millivoltmeter; thus temperature determination may become accurate to  $0.1^{\circ}\text{C.}$  over a large temperature range.

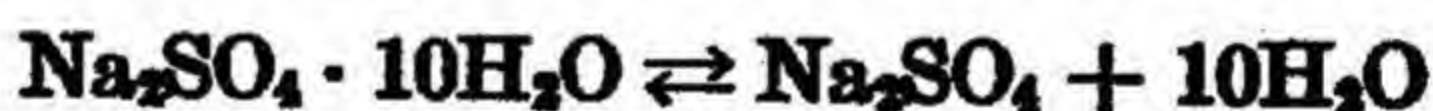


*Amel*

## EXPERIMENT 24

### DETERMINATION OF TRANSITION POINT

The temperature at which two different hydrates of a salt are in equilibrium, or at which any two polymorphic forms are in equilibrium (the transition point), may be determined very simply by the thermometric method, if the transformation of one form to the other takes place fairly rapidly. Numerous examples of transition points are known. For instance, there is the change of rhombic into monoclinic sulfur (at  $95.6^{\circ}$ ); or the change of non-rotating  $\text{CH}_4$  molecules to rotating molecules, in the crystal lattice at about  $-253^{\circ}\text{C.}$ ; or the change of  $\alpha$ -iron, *body-centered cubic* lattice, into  $\gamma$ -iron, *face-centered cubic*, etc. In the present experiment the transition point of the transformation



will be determined.

#### EXPERIMENTAL

Place about 30 g. freshly crystallized  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  in a thin glass test tube, which is held by a cork inside a larger test tube with an air jacket in between, or better place the salt in an unsilvered Dewar test tube, and push the bulb of a thermometer graduated in  $0.1^{\circ}$  down into the salt. Support this tube in a large beaker of water which is very gradually heated with a small gas flame. Stir the water constantly and let the temperature rise (to about  $34^{\circ}$ ) until the salt melts. Now remove the flame from the water-bath, and as the bath slowly cools, constantly about  $5^{\circ}$  below the temperature of the transition substance, stir the molten salt with a small glass rod curved at the lower end into a loop which may be made to slide up and down over the thermometer bulb. The bulb should be completely covered by the melt. Take temperature readings every minute and plot the temperature (ordinate) against time (abscissa). At about the transition point a crystal of the decahydrate may be introduced to facilitate the formation of the hydrated salt. The flat portion of the curve (the transition point)



corresponds to a condition in which the rate of generation of heat by the hydration of the anhydrous salt is just balanced by the rate of thermal leakage by radiation, conduction, etc.

After the melt has solidified, again warm the water-bath gradually, again about  $5^{\circ}$  in advance of the transition substance, and while constantly stirring the salt, and plotting the observed temperature against time, determine the transition point with rising temperature. When the melt is first cooled it solidifies in a fine crystalline mass, which is much more readily stirred than the large crystals initially introduced into the tube. For this reason it is best to determine the transition point with falling temperature first.

Repeat both determinations, and take the mean of the averages of the initial points of inflection on the two rising temperature curves, and of the horizontal positions on the two falling temperature curves as the transition point. The temperature of this transition is so easily reproducible ( $32.383^{\circ}$ ) that it is often employed as one of the fixed temperature points in the standardization of mercury thermometers, as well as other thermometric instruments.

The success of this experiment depends on controlling the rate of heat input and outflow so that the transition substance is kept at the transition temperature for a long time.

#### REFERENCES:

- Taylor, Chap. X.
- Rodebush, Chap. VI.
- Getman and Daniels, Chap. XIII.
- Millard, Chap. IX.
- Findlay, Chap. XIX.



## EXPERIMENT 25

### DISTRIBUTION COEFFICIENT

If a solvent with a solute in solution is brought into contact with a second solvent, which is immiscible with the first solvent, or only partially miscible, but in which the solute will also dissolve, a distribution of the solute between both solvents will occur. Moreover, the ratio of the concentrations of the solute in the two solvents will be a constant, regardless of the actual concentrations. This relationship may be expressed symbolically by the equation

$$\frac{c_1}{c_2} = K \quad (1)$$

where  $K$  is known as the distribution coefficient. It varies with the nature of the solute and the nature of the solvents, and also with temperature. The concentrations  $c_1$  and  $c_2$  are in the same proportion as the solubilities of the solute in the two solvents taken separately. Equation 1 is Nernst's partition law; it is essentially a form of Henry's law. Equation 1 is true only if the solute has the same molecular weight in both solvents. If the solute has its normal molecular weight,  $M$ , in one solvent but is polymerized, say to  $M_2$ , in the other solvent, then

$$\frac{c_M}{\sqrt{c_{M_2}}} = K. \quad (2)$$

Let the student derive Equation 2 from Equation 1 and from a consideration of the law of mass action.

A convenient system often employed for demonstrating the validity of Equation 1 is that involving the distribution of succinic acid,  $\text{COOH}(\text{CH}_2)_2\text{COOH}$ , between water and ether, and determining the equilibrium concentrations analytically by titration with  $\text{Ba}(\text{OH})_2$  solution. In the present experiment, however, we shall study the distribution of iodine between water and chloroform (or carbon tetrachloride). In order to increase the solubility of the iodine in the water phase, we shall add some potassium iodide ( $\text{KI}$ ) to the water. While it is true that the  $\text{I}_2$



molecules react with iodide ions ( $I^-$ ) to form  $I_3^-$ , yet the molecular weight of the iodine itself may be considered not to have changed, thus  $I_2 \cdot I^-$ ; that is, the KI solution may be considered as being the solvent, rather than the water alone. As long as the strength of the KI solution is not altered during the course of the experiment, it may be thought of as being a pure, single-substance solvent, and Equation 1 should be valid. It is the purpose of the present experiment not only to determine the value of the distribution coefficient,  $K$ , for  $I_2$  in the system chloroform-KI solution, but also to study the relative efficiency of extraction of iodine with a given volume of chloroform, (1) using all the chloroform in one portion, and (2) in several portions.

If  $W$  cc. of a solution containing  $x_0$  g. of solute be extracted with  $nL$  cc. of a given solvent, the residue unextracted may be represented by  $x_1$ . The concentration in the extracted solution is then  $\frac{x_1}{W}$ , and in the extracting phase  $\frac{x_0 - x_1}{nL}$ . The distribution coefficient  $K$  is therefore

$$K = \frac{\frac{x_1}{W}}{\frac{x_0 - x_1}{nL}} \quad (3)$$

from which it follows that

$$\frac{nL}{KW} = \frac{x_0 - x_1}{x_1}$$

and

$$\frac{nL + KW}{KW} = \frac{(x_0 - x_1) + x_1}{x_1} = \frac{x_0}{x_1}$$

and hence

$$x_1 = \frac{KW}{nL + KW} x_0 \quad (4)$$

This equation gives  $x_1$ , the amount unextracted, in terms of  $x_0$ , the amount originally present.

Now let us suppose that instead of using the total quantity  $nL$  cc. in a single extraction, we divide the solvent into  $n$  portions and use  $L$  cc. successively for  $n$  extractions. After the first extraction the amount unextracted would be

$$x_1 = \frac{KW}{L + KW} x_0$$



If now a second portion of  $L$  cc. were used, the amount unextracted would be

$$x_2 = \frac{KW}{L + KW} x_1 = \frac{KW}{L + KW} \cdot \frac{KW}{L + KW} x_0 = \left( \frac{KW}{L + KW} \right)^2 x_0$$

Generalizing, after  $n$  extractions with  $L$  cc. the residue unextracted would be

$$x_n = \left( \frac{KW}{L + KW} \right)^n x_0 \quad (5)$$

(See Knox, *Physico-Chemical Calculations*, Chap. 8, Van Nostrand.)

#### EXPERIMENTAL

With a calibrated pipette take 10 cc. of a 4 per cent aqueous solution of potassium iodide which has been saturated with iodine and with chloroform (since chloroform is slightly soluble in water), and titrate it with standard thiosulfate solution approximately 0.02  $N$  (with starch paste as indicator). Repeat the titration as a check. Now shake 50 cc. of the iodine solution in a separatory funnel with 50 cc. of chloroform, separate the two layers and titrate 10 cc. of the aqueous layer, again repeating as a check. Using Equation 1 calculate the distribution coefficient.

Shake 50 cc. of the iodine solution with 25 cc. of chloroform in the separatory funnel, and again calculate  $K$ . Since in this case the final equilibrium concentration of iodine in the aqueous phase must necessarily be greater than before, the constancy of  $K$  is tested at a different concentration. Repeat, using 50 cc. of the iodine solution and 12.5 cc. of chloroform. Take the average of the three calculations as the value for the distribution coefficient, and in obtaining the average give a weight of 4 to the result with 50 cc., of 2 to the result with 25 cc., and of 1 to the 12.5 cc. result.

Dilute 10 cc. of the iodine solution to 50 cc. with distilled water (which has been saturated with chloroform), shake with 50 cc. chloroform in the separatory funnel, and again determine  $K$ . Has it the same value as before? Explain.

Pour 50 cc. of the iodine solution into the separatory funnel, and shake it with five successive portions of chloroform of 10 cc. each. Draw off the chloroform after each shaking and titrate the chloroform with thiosulfate solution. (In titrating, take care to



shake vigorously after each addition of thiosulfate.) What is the amount of iodine finally left unextracted? Check, by titrating the final aqueous solution. How much more efficient is the portion-wise extraction than the extraction using the whole 50 cc. volume of chloroform at one time?

Using Equation 5, calculate  $x_5$  for the portion-wise extraction, and compare the predicted result with the experimental result.

An interesting Boltzmann factor treatment can be given to the distribution of iodine between the two liquid phases. First calculate for a given KI concentration, the actual or relative numbers of  $I_2$  molecules in 1 cc. of each solvent, figured as  $I_2 \cdot I'$  molecules in the KI solution and as  $I_2$  molecules in the  $CHCl_3$ . Then,

$$\frac{n_{I_2 \cdot I'}}{n_{I_2}} = e^{-\frac{W}{RT}} = K \text{ (distribution coefficient)}$$

where  $W$  is the work required to remove a mol of  $I_2$  from the  $CHCl_3$  into the KI solution. Calculate  $W$  for the distributions between  $CHCl_3$  and both of the two KI solutions of different concentrations. (See Exercise III.)

#### REFERENCES.

- Taylor, Chap. X.
- Rodebush, Chap. VII.
- Getman and Daniels, Chap. XIII.
- Millard, Chap. V.
- Findlay, Chap. XVIII.



## EXPERIMENT 26

### AN ION REACTION: VELOCITY; ORDER OF REACTION; TEMPERATURE COEFFICIENT; CATALYSIS; AND BRÖNSTED THEORY

It is generally true that organic molecules at convenient temperatures undergo chemical reaction slowly enough to give easily measurable rates of reaction. But the reactions between ions, for example,  $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$ , are usually extremely rapid, so rapid indeed that it becomes difficult to measure the rate experimentally. Occasionally, however, we encounter ion reactions which are slow. These slower ion reactions generally involve an internal rearrangement of atoms within the ion during the course of the reaction and not merely the pairing off of oppositely charged ions as in the formation of  $\text{AgCl}$ . Such an ion reaction has been chosen for study in the present experiment, namely a reaction of potassium iodide and potassium persulfate in aqueous solution to form free iodine (investigated by T. S. Price, *Z. phys. Chem.*, **27**, 474 (1898)):



The reaction involves the transfer of 2 electron from  $2\text{I}^-$  to the persulfate ion,  $\text{S}_2\text{O}_8^{2-}$ , accompanied by the splitting of this ion into two sulfate ions,  $\text{SO}_4^{2-}$  and the union of  $2\text{I}$  atoms to form  $\text{I}_2$ . This reaction lends itself very satisfactorily to the illustration of a number of the important factors which in general operate to control the velocity of chemical reactions. We shall now give directions for this experiment, and at suitable points introduce a little theoretical background.

#### EXPERIMENTAL

The course of the reaction is followed by titration of the liberated iodine with 0.01 *N* sodium thiosulfate solution ( $\text{Na}_2\text{S}_2\text{O}_3$ ) with starch paste as indicator. An ordinary 50 cc. burette will be needed for the thiosulfate solution and also a 1 cc. pipette, graduated in 0.01 cc., and rigged up to serve as a burette by at-



tachment of a glass exit tip by means of a short length of rubber tubing which can be squeezed with a thumb clamp (in lieu of a glass stop-cock). Now obtain from the instructor, or prepare, 1000 cc. of 0.1 *N* KI solution, and 1000 cc. 0.1 *N*  $K_2S_2O_8$  solution, made from freshly recrystallized potassium persulfate. The recrystallization is necessary because the  $K_2S_2O_8$  taken from the stock bottle generally has decomposed a little to give  $SO_4^{=}$ . Both of these solutions must be made up freshly at the time of the experiment from *crystals* of KI and  $K_2S_2O_8$ , since the solutions decompose appreciably on standing for even 24 hours.

#### (A) VELOCITY CONSTANT AND ORDER OF REACTION

(1) Pipette 100 cc. of the 0.1 *N* KI solution into a beaker and 100 cc. of the 0.1 *N*  $K_2S_2O_8$  solution into another beaker or Erlenmeyer flask large enough to hold 200 cc. Then pour the KI solution into the  $K_2S_2O_8$  solution, so that the total volume of the mixture is 200 cc., and the normality of each salt becomes 0.05. Stir thoroughly with a glass rod and allow the reaction to proceed at room temperature. Note the temperature. Also note the time of mixing, on a stop watch or on a watch with a *second* hand. The color soon becomes yellow and then brownish, due to the liberation of iodine. At 5 minute intervals pipette out 25 cc. of the reaction mixture and titrate as rapidly as possible with 0.01 *N* sodium thiosulfate solution in the 50 cc. burette (using starch near the end point). Continue the titrations for 30–40 minutes. Run this experiment in duplicate. The second reaction mixture may be made up 2 or 3 minutes after the first one, and the titrations staggered.

(2) Repeat at room temperature, but take the proper volumes of 0.1 *N* KI and 0.1 *N*  $K_2S_2O_8$  solutions to give 0.02 *N* solution of each when they are mixed with distilled water and brought to a total volume of 200 cc. Again run in duplicate, and in this case titrate 25 cc. samples taken at about 10 minute intervals for about an hour. Use the 1 cc. burette.

(3) Repeat at room temperature, but take the proper volumes of 0.1 *N* KI and 0.1 *N*  $K_2S_2O_8$  solutions to give 0.01 *N* solution of each when the reaction mixture is made up to a total of 200 cc. volume. Again the reaction mixture may be sampled and titrated at about 10 minute intervals for 60–80 minutes.



In determining the "order" of this reaction the student should consult the discussion on functional relationships in Exercise III. The student is asked to demonstrate that this is a bimolecular reaction by three different methods of treating the data. One might suppose, from the chemical equation, that this reaction would be trimolecular. But in general one cannot guess the order of a reaction from the stoichiometric relationships of the balanced chemical equation.

(a) First, let us start with the hypothesis that the reaction is bimolecular (second order, as indeed it is, at least approximately). The general differential equation for a bimolecular reaction is

$$\frac{dx}{dt} = k(a - x)(b - x) \quad (1)$$

where  $x$  is the change in concentration in gram-equivalents at any time  $t$ , and  $a$  and  $b$  are the initial concentrations of the two different molecular species reacting with one another,  $A$  and  $B$ , and  $k$  is the velocity constant. If the initial concentrations  $a$  and  $b$  of these two substances are the same (in gram-equivalents), then Equation 1 reduces to the form

$$\frac{dx}{dt} = k(a - x)^2 \quad (2)$$

When this equation, which may be written  $\frac{dx}{(a - x)^2} = kt$ , is integrated, we get

$$\frac{1}{(a - x)} = kt + C \quad (3)$$

and when  $t = 0$ , the integration constant  $C = \frac{1}{a}$ . Therefore,

$$\frac{1}{(a - x)} - \frac{1}{a} = kt$$

or

$$k = \frac{1}{t} \frac{x}{a(a - x)} \quad (4)$$

The test of the validity of Equation 4 for any reaction, suspected of being bimolecular, is the *constancy* of  $k$ . Since, in the present experiment, the concentrations of  $I^-$  and  $S_2O_8^{2-}$  have been pur-



posely made the same, it is easy to calculate  $x$ , the concentration of either  $I^-$  or  $S_2O_8^{2-}$  which has reacted (suppose we take  $I^-$ ), and  $(a - x)$  the concentration in the system at any time  $t$ , from the observed amounts of  $I_2$  liberated. Make up three tables, one for 0.05  $N$ , one for 0.02  $N$  and one for 0.01  $N$  solutions. In the first column of each one list the different values of  $t$ , in the second column values for  $x$ , in the third values for  $(a - x)$ , and in the fourth calculated values for  $k$  (from Equation 4). These values of  $k$  should be fairly consistent within each table, and approximately the same for the three different tables, although not exactly the same, as will be explained later in Section D. Thus, while the actual *velocity* of the reaction is less in (3) above, with the 0.01  $N$  solutions, than in (2) with the 0.02  $N$  solutions, and less in (2) than in (1) with the 0.05  $N$  solutions, illustrating the law of mass action, the values of  $k$  are substantially the same in all three cases.

(b) The order of the reaction may be established in another way. If the half-life time,  $t_{\frac{1}{2}}$ , at the end of which the reaction is one-half completed, is calculated from Equation 4, above, we get

$$t_{\frac{1}{2}} = \frac{1}{k} \cdot \frac{a/2}{a(a - a/2)} = \frac{1}{k} \cdot \frac{1}{a}.$$

In other words the half-life of a bimolecular reaction is inversely proportional to the initial concentration of one of the two substances present in equivalent proportions. Therefore the half-life should be twice as long in (3) than in (2) and five times as long in (2) than in (1). Calculate the half-life for these foregoing three concentrations, or determine it by interpolation from the observed data, and employ this criterion to test whether or not the reaction is second order.

(c) In general the order of a chemical reaction may be determined by plotting a properly chosen function of the concentration against time. For example, for a bimolecular reaction,  $\frac{x}{a(a - x)}$  from Equation 4, plotted against the time,  $t$ , will give a straight line of positive slope  $k$ . Or, a plot of  $\frac{1}{(a - x)}$  against  $t$  from

Equation 3,  $\frac{1}{(a - x)} = kt + C$ , will give a straight line of positive slope  $k$ , with an intercept  $C$ .



**(B) VELOCITY AS A FUNCTION OF TEMPERATURE**

Chemical reactions generally go more rapidly as the temperature is increased. The conventional method of expressing a temperature coefficient is to designate it as the ratio of the velocity constant at one temperature to the constant at a temperature  $10^{\circ}\text{C}$ . lower.

In the present study of chemical reaction velocity as a function of temperature we shall use the more concentrated  $0.05\text{ N}$  solutions, in order to obtain results without taking too long a time. The velocity of this reaction has been studied at room temperature already, in the foregoing pages.

Place  $100\text{ cc. } 0.1\text{ N KI}$  solution and  $100\text{ cc. } 0.1\text{ N K}_2\text{S}_2\text{O}_8$  solution, respectively, in two Erlenmeyer flasks, and immerse these flasks in some finely crushed ice. When the temperature of both solutions has attained  $0^{\circ}$ , as shown on a thermometer, mix them together in one of the flasks, and allow the reaction to proceed in the ice-bath. Withdraw  $25\text{ cc.}$  at regular time intervals as before and titrate with  $0.01\text{ N}$  sodium thiosulfate solution, using the  $50\text{ cc.}$  burette. Run in duplicate.

Repeat at a temperature of about  $40^{\circ}\text{--}45^{\circ}$ . If an automatically controlled water thermostat operating at this temperature is not available, a large beaker or a large cooking pot filled with water and maintained as nearly as possible at constant temperature by hand regulation, will be satisfactory.

Calculate the velocity constant  $k$ , as before, at both temperatures. The constants at  $0^{\circ}$ , at room temperature, and at about  $40^{\circ}$  are now known. Calculate the average temperature coefficient.

The relationship between the velocity constant and temperature is an interesting one. The most useful present idea regarding this relationship was proposed by Arrhenius, and may be presented in the following way. A natural question which occurs in connection with slow reactions, either between molecules or ions, is that of why the reactions, if they can occur at all, do not take place instantly, as in the case of rapid ion reactions. Arrhenius suggested the idea that the reacting particles, in addition to the requirement of having to come into actual contact with one another by collision, must also be endowed with a certain char-



acteristic minimum energy content sufficiently large to loosen up the internal structure of the particle, and permit it to undergo the internal atomic rearrangements which result in the accomplishment of the chemical act. For example, two colliding particles would have to collide with a sufficiently shattering force to disrupt either one or both; otherwise they would simply bounce off, and no chemical reaction would occur. In other words, not all collisions lead to chemical reaction; in fact the percentage of effective collisions is usually extraordinarily small, because the minimum "energy of activation" (as it is called) is usually fairly large. The distribution of energy in a swarm of particles follows the Maxwell-Boltzmann law. Only a relatively few molecules at a given instant are *richly* endowed with kinetic energy. The fraction of the total number of molecules which possess energy equal to or greater than any value  $E$ , the characteristic energy of activation, is given by the Boltzmann factor,  $e^{-\epsilon/k_b T}$ , or  $e^{-E/RT}$ , where  $\epsilon$  and  $E$  are the energy of the activation per molecule and per mol,  $T$  is the absolute temperature, and  $k_b$  and  $R$  are the Boltzmann molecular constant and the molar gas constant, respectively. (See the discussion of the Boltzmann factor in Exercise III.)

According to Arrhenius' hypothesis the velocity constant,  $k$ , of a chemical reaction would be proportional *both* to the number of collisions between reactant particles and to the fraction of the total number of particles possessing energy of activation; or in symbols,

$$k = \text{Const.} \times \text{no. collisions} \times e^{-E/RT}.$$

Since the number of collisions does not vary greatly with changing temperature, we may write

$$k = C \cdot e^{-E/RT}.$$

Taking logarithms of both sides we get

$$\ln k = \ln C - \frac{E}{RT}. \quad (5)$$

If we then differentiate to get the rate of variation of  $k$  with  $T$ , we have

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}.$$

This is the famous Arrhenius equation, although Arrhenius derived



it in a somewhat different manner. Upon integration between limits, on the assumption that  $E$  is independent of temperature,

$$\ln \frac{k_1}{k_2} = \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right). \quad (6)$$

Now calculate  $E$  the energy of activation (per mol) for the ion reaction which we are studying, by two different methods. First, use Equation 6, with the velocity constants actually found at the three different temperatures. Second, convert the natural logarithms of Equation 5 to Briggsian logarithms, namely,

$$\log k = \log C - \frac{E}{2.3 RT}$$

and by plotting  $\log k$  against  $\frac{1}{T}$ , determine the value of the slope  $\frac{E}{2.3 R}$  graphically and from it calculate  $E$ . The straight line relationship of course indicates that  $E$  is really constant, and is independent of temperature, at least over this range. For convenience in plotting, the reciprocal of the *absolute* temperature,  $\frac{1}{T}$ , may be multiplied by  $10^3$ , and the number 6 may be added to the logarithms of the three  $k$ 's to give positive numbers.

From the value of  $E$  calculate the Boltzmann factor, i.e., the fraction of the total number of molecules (or really of the total number of collisions) which possess energy of activation. In the case of some bimolecular reactions in the *gas phase* it has been possible to calculate both the Boltzmann factor and the number of collisions between molecules in unit time, and hence to calculate the absolute value of  $k$  on theoretical grounds. Some of these calculated values agree remarkably well with the observed values for  $k$ . But in the case of chemical reactions in a *liquid* medium, it is much more difficult to estimate the number of collisions, and as yet no encouraging agreement has been obtained between calculated and observed absolute values of  $k$ .

### (C) CATALYSIS

To use our present ion reaction as a medium for illustration of a catalytic effect, the student may perform the following experiment. Repeat the determination of the velocity constant with



0.01 *N* solutions, as in A (3) above at room temperature with four separate reaction mixtures, using one as a control, and adding enough  $\text{CuSO}_4$  solution of convenient strength (say 0.01 *M*) in diluting the stock 0.1 *N*  $\text{KI}$  and 0.1 *N*  $\text{K}_2\text{S}_2\text{O}_8$  solutions to 200 cc. to make one mixture  $\frac{M}{8000}$  with respect to  $\text{CuSO}_4$ , one  $\frac{M}{4000}$  and the other  $\frac{M}{2000}$ . Withdraw 25 cc. samples, as before, titrate, and calculate the velocity constants *k*. Plot *k* as ordinate against  $\text{CuSO}_4$  concentration as abscissa.

It will be noticed that the very considerably augmented velocity constant is directly proportional to the concentration of the  $\text{Cu}^{++}$  catalyst. Other ions, such as  $\text{Fe}^{++}$ , also catalyze this reaction. No completely satisfying explanation has yet been given of homogeneous catalysis of this type. As we have already indicated, molecules or slowly reacting ions must pass over certain "potential barriers," or acquire certain minimum energies of activation, or be sufficiently profoundly disturbed or disrupted internally, before they will undergo chemical reaction. It may be possible that the copper ions,  $\text{Cu}^{++}$  become associated with the  $\text{S}_2\text{O}_8^{=}$  ions in a loose chemical complex of such a sort that the electrostatic force field of the  $\text{Cu}^{++}$  strains or distorts the internal structure of the  $\text{S}_2\text{O}_8$  ion and makes it more fragile and more reactive chemically. After the chemical change occurs the  $\text{Cu}^{++}$  is set free. Or it may be that the  $\text{Cu}^{++}$  ion, because of its ability to go over into a lower valence state,  $\text{Cu}^+$ , may play the rôle of assisting in the transfer of electrons from  $\text{I}^-$  to  $\text{S}_2\text{O}_8^{=}$ . Both of these ideas have here been expressed in very general language. We are not justified in attempting to commit ourselves to any clear-cut, definite picture of the details of the mechanism, in the present state of our knowledge. But it is possible that something of this general sort operates to speed up the velocity of the reaction.

#### (D) BRÖNSTED'S THEORY OF ION REACTIONS

The ion reaction between  $\text{I}^-$  and  $\text{S}_2\text{O}_8^{=}$  which we are studying in the present chapter lends itself very beautifully to the illustration of the new theory of Brönsted. We shall first give a brief résumé of the points of this theory, and then give directions for the experiment.



It was recognized many years ago that the usual law of mass action, stated in the form,

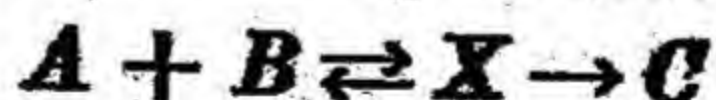
$$\frac{dx}{dt} = k \cdot c_A \cdot c_B \quad (7)$$

where  $c_A$  and  $c_B$  represent the concentration or active mass of the reacting ions  $A$  and  $B$ , does not hold for electrolytes, i.e., for ion reactions. Later the function "activity" was defined, and it was defined as that function which, when used in the equilibrium equation  $K = \frac{a_{AB}}{a_A \cdot a_B}$ , would make the equilibrium equation work, even for ionic equilibrium. Then it was supposed that this concept of activity taken out of its equilibrium setting and extended to the problem of *velocities* of chemical reactions, would lead to a statement of the law of mass action in the form,

$$\frac{dx}{dt} = k \cdot a_A \cdot a_B \quad \text{or} \quad \frac{dx}{dt} = k \cdot \gamma_A \cdot c_A \cdot \gamma_B \cdot c_B \quad (8)$$

where  $a$  represents activity and  $\gamma$  represents activity coefficient, and that then the former difficulties of the application of the mass action principle to ion reactions would disappear. But this expectation was not justified. Many startling discrepancies were still found. In general  $k$ , which ought to have been a constant throughout the course of a reaction, regardless of the ion concentrations, was *not* constant. In view of these difficulties, Brønsted has suggested a new type of approach to the problem. (The student may consult a lecture on this subject in Brønsted's own words in the Columbia Lecture Series "Contemporary Developments in Chemistry," Columbia University Press, 1927.)

When  $A$  and  $B$  ions react to form product  $C$ , let us suppose that  $A$  and  $B$  must pass through an intermediate critical state (we have already spoken of energy of activation), but in the case of ion reactions we may suppose that some sort of complex,  $X$ , of unknown nature, is formed by the association of  $A$  and  $B$ , and that this complex then undergoes rearrangement to give the product  $C$ . If  $A$  and  $B$  are in equilibrium with  $X$  then



and the equilibrium constant  $K$  may be written

$$K = \frac{a_X}{a_A \cdot a_B} = \frac{\gamma_X \cdot c_X}{\gamma_A \cdot c_A \cdot \gamma_B \cdot c_B} = \frac{\gamma_X}{\gamma_A \cdot \gamma_B} \cdot \frac{c_X}{c_A \cdot c_B}$$



Now on the further assumption that the velocity of the final chemical transformation is directly proportional to the concentration of the complex  $X$ , we have

$$\frac{dx}{dt} = k \cdot c_X.$$

But, since

$$c_X = K \cdot c_A \cdot c_B \cdot \frac{\gamma_A \cdot \gamma_B}{\gamma_X}, \text{ then } \frac{dx}{dt} = k \cdot c_A \cdot c_B \cdot \frac{\gamma_A \cdot \gamma_B}{\gamma_X}. \quad (9)$$

This equation differs from Equation 7 (the classical expression) by the factor  $\frac{\gamma_A \cdot \gamma_B}{\gamma_X}$ , and from Equation 8 (the activity expression)

by the factor  $\frac{1}{\gamma_X}$ . Further, since  $c_A$  and  $c_B$ , the concentrations of the ions, can be determined in any reacting system by methods of quantitative analysis, the next step in the development of the Brönsted argument involves the necessity of evaluating the factor  $\frac{\gamma_A \cdot \gamma_B}{\gamma_X}$ . This can be done with the equation

$$-\log \gamma = 0.5 z^2 \sqrt{\mu} \quad (10)$$

where  $\gamma$  is the activity coefficient of the ion,  $z$  its valence and  $\mu$  is the so-called "ion-strength." This function  $\mu$  is defined as

$$\mu = \sum 1/2 m z^2; \text{ or } \mu = \sum 1/2 c z^2$$

where  $m$  is the molal and  $c$  the equivalent concentration of the ion; i.e.,  $\mu$  is the sum of  $1/2$  of all the molal concentrations multiplied by the valence squared for all of the ions present in the solution. Equation 10 holds only for extremely dilute solutions. It is derived from the Debye-Hückel Theory of ion solutions. (A development of this theory is beyond the scope of this manual; but the student may consult the references at the end of this chapter.)

Using Equation 10 we can find the value of the logarithm of the factor  $\frac{\gamma_A \cdot \gamma_B}{\gamma_X}$  in Equation 9:

$$\begin{aligned} \log \frac{\gamma_A \cdot \gamma_B}{\gamma_X} &= -0.5 z_A^2 \sqrt{\mu} - 0.5 z_B^2 \sqrt{\mu} + 0.5 z_X^2 \sqrt{\mu} \\ &= -0.5 (z_A^2 + z_B^2 - z_X^2) \sqrt{\mu}. \end{aligned}$$



Now, since the valence of the complex  $X$  is the algebraic sum of the valencies of the ions  $A$  and  $B$  which form the complex, i.e.,  $z_X = z_A + z_B$  it follows that

$$\log \frac{\gamma_A \cdot \gamma_B}{\gamma_X} = -0.5 [z_A^2 + z_B^2 - (z_A + z_B)^2] \sqrt{\mu} = z_A \cdot z_B \sqrt{\mu}$$

Hence

$$\frac{\gamma_A \cdot \gamma_B}{\gamma_X} = 10^{z_A z_B \sqrt{\mu}}$$

and from Equation 9,

$$\frac{dx}{dt} = k \cdot c_A \cdot c_B \cdot 10^{z_A z_B \sqrt{\mu}} \quad (11)$$

This fairly simple equation gives the velocity of a bimolecular ion reaction, between  $A$  and  $B$ , in extremely dilute solutions. It is to be remembered that the velocity constant  $k$  in Equation 11 is the actually observed velocity constant, calculated as in the previous sections (A), (B) and (C) from Equation 1; i.e.  $k$  itself is calculated on the classical basis,  $\frac{dx}{dt} = k \cdot c_A \cdot c_B$ . The constant  $k$  itself is,

however, proportional to  $\frac{\gamma_A \cdot \gamma_B}{\gamma_X}$ . This follows from Equation 9.

If the function  $\frac{\gamma_A \cdot \gamma_B}{\gamma_X}$  is 1 (unity), Equation 9 reduces to the classical Equation 1. The term  $\frac{\gamma_A \cdot \gamma_B}{\gamma_X}$  may be regarded as a corrective factor for  $k$ . The larger it is, the larger  $k$  will be; the smaller it is, the smaller  $k$  will be. Hence

$$k = \text{Const.} \frac{\gamma_A \cdot \gamma_B}{\gamma_X} = \text{Const.} 10^{z_A z_B \sqrt{\mu}}$$

This relationship provides us with a convenient method for testing the validity of Equation 11. For, if we take logarithms,

$$\log k = \log \text{Const.} + z_A z_B \sqrt{\mu}$$

a plot of  $\log k$  against  $\sqrt{\mu}$  should give a straight line of slope  $z_A \cdot z_B$ . If the valence of  $A$  is  $+1$  and of  $B$  is  $+1$ , i.e., if  $z_A = +1$ , and  $z_B = +1$ , then the slope  $z_A \cdot z_B$  would be  $+1$ . This means that the  $\log k$  or  $k$  itself will become greater with increasing ion strength, since  $\sqrt{\mu}$  becomes larger with increasing  $\mu$ . It does not make any



difference whether the increase in ion strength is due to an increase in the concentration of the reacting ions themselves, or to added neutral salt, or both. Such an increase in the value of  $k$  produced in a solution of increased ion strength is called a "positive salt effect." On the other hand if  $z_A = +1$  and  $z_B = -1$ , the slope is  $= -1$ , and the salt effect is negative; i.e.,  $k$  is diminished by increasing ion strength, and the reaction goes more slowly. If  $z_A = -2$  and  $z_B = +1$ , the slope is  $-2$ . If  $z_A = -2$  and  $z_B = -2$ , the slope is  $+4$ ; etc.

In our present bimolecular reaction, between  $I^-$  and  $S_2O_8^{2-}$   $z_A = -1$  and  $z_B = -2$ ; therefore  $z_A \cdot z_B$ , the slope, would be  $+2$ . If a plot of  $\log k$  against  $\sqrt{\mu}$  actually gives a slope of  $+2$ , we may consider that there is good reason for believing that Brönsted's theory is substantiated in the present case, and also that the chemical process really involves the reaction of  $I^-$  and  $S_2O_8^{2-}$ .

The student may now perform the following experiment. Run, in duplicate, at room temperature, a determination of the velocity constant with 200 cc. total volume of mixture 0.01  $N$  with respect to  $KI$  and  $K_2S_2O_8$ , as before, in A (3). But, instead of making the proper dilutions with distilled water, use 4  $N$   $NaCl$  solution. It will be noted that the reaction velocity is much faster than before, i.e., that there is a positive salt effect, as predicted. Furthermore, it will be noted that the values of the bimolecular constant  $k$ , while larger than before, are much more constant and consistent. Excellent values of  $k$  are now obtained. The point, of course, is that the ion strength in the system is so great, in this strong salt solution, that any small irregularities formerly introduced into the system by the changing activity coefficients which result from changing interionic forces which result from changes in ion concentrations during the course of the reaction, are now drowned out.

Repeat the determination, again with 0.01  $N$   $KI$  and 0.01  $N$   $K_2S_2O_8$ , but this time use both 4  $N$   $NaCl$  solution and distilled water, so that the final concentration of  $NaCl$  in the 200 cc. of mixture is half what it was before.

Repeat again, and make the  $NaCl$  concentration a quarter of what it was in the first salt experiment.

Now plot  $\log k$  (as ordinate) against  $\sqrt{\mu}$  (as abscissa). There will be six points to plot, i.e., six different  $\log k$ 's and six different



ion strengths,  $\mu$  (and  $\sqrt{\mu}$ ) to be figured: (1) 0.01 *N* mixture without salt, (2) 0.02 *N* mixture without salt, (3) 0.05 *N* mixture without salt, all results obtained in A, and (4), (5), (6), the three mixtures with added salt. If desired, one may also make other determinations in which such salts as  $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$ , etc. are added. In every case a positive salt effect will be found. In order to illustrate the calculation of the ion strength,  $\mu$ , we may consider one of the above six solutions. Let us take (4), the one in which the full strength 4 *N*  $\text{NaCl}$  is used for the dilution. The ion strength is figured on the basis of 100% ionization. Since the  $\text{KI}$  is 0.01 *N* (or 0.01 *M*),  $1/2 m z^2$  for  $\text{K}^+ = 1/2 \times 0.01 \times 1^2 = 0.005$ ; for  $\text{I}^-$ ,  $1/2 m z^2 = 1/2 \times 0.01 \times 1^2 = 0.005$ . The  $\text{K}_2\text{S}_2\text{O}_8$  is 0.01 *N* (or 0.005 *M*). Then for  $\text{S}_2\text{O}_8^{2-}$ ,  $1/2 m z^2 = 1/2 \times .005 \times 2^2 = 0.01$ ; and for  $2\text{K}^+$ ,  $1/2 m z^2 = 1/2 \times 0.01 \times 1^2 = 0.005$ . Since 20 cc. of each of the solutions 0.1 *N*  $\text{KI}$  and 0.1 *N*  $\text{K}_2\text{S}_2\text{O}_8$ , and

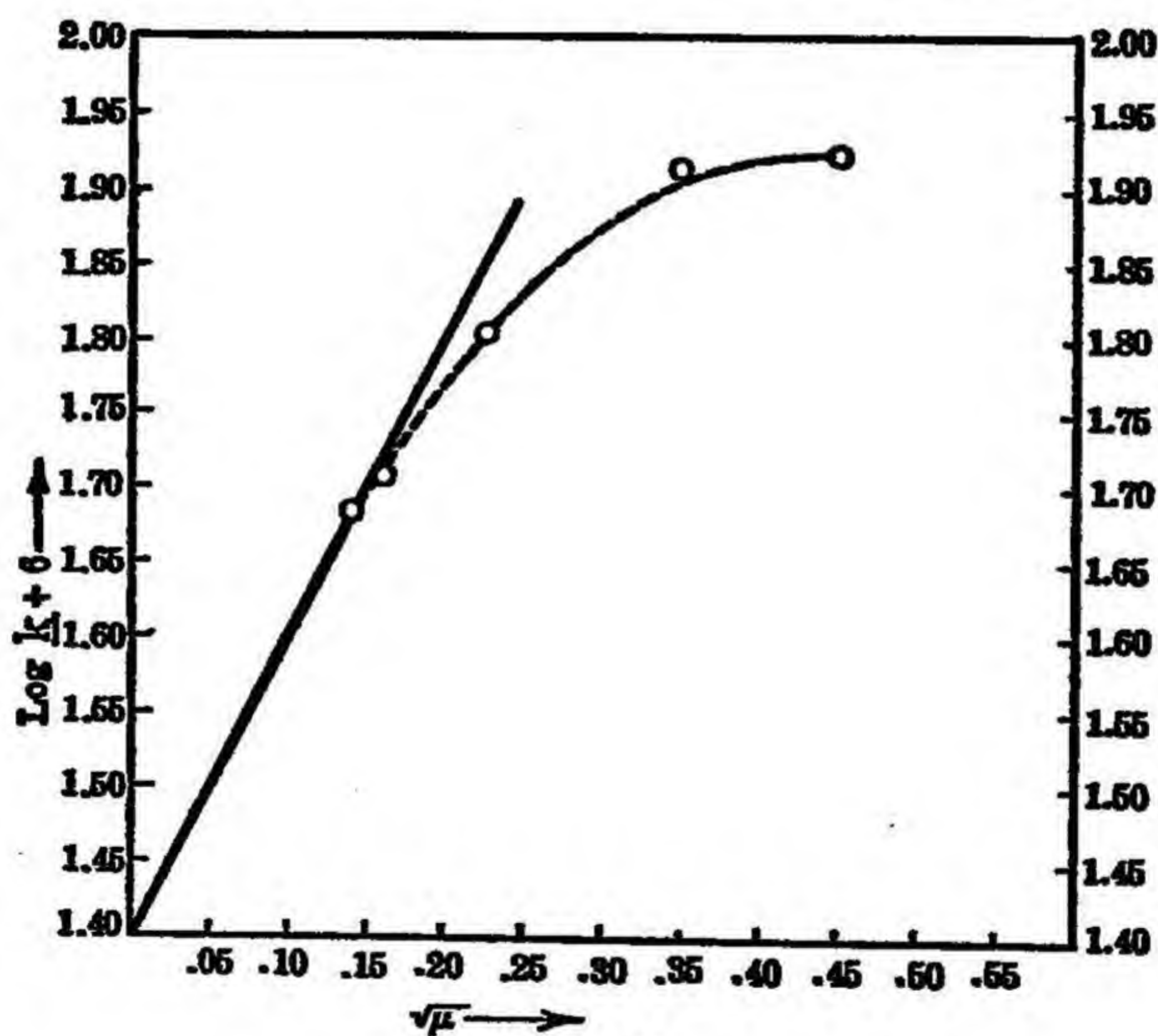


FIG. 47

160 cc. of 4 *N*  $\text{NaCl}$  are used to make up the 200 cc., the concentration of the  $\text{NaCl}$  in the final solution is  $\frac{160}{200} \times 4 \text{ M} = 3.2 \text{ M}$ . Hence  $1/2 m z^2$  for  $\text{Na}^+ = 1/2 \times 3.2 \times 1^2 = 1.6$  and  $1/2 m z^2$  for  $\text{Cl}^- = 1/2 \times 3.2 \times 1^2 = 1.6$ . Therefore  $\sum 1/2 m z^2 = 0.005 + .005 + .01 + .005 + 1.6 + 1.6 = 3.225 = \mu$ . Then  $\sqrt{\mu} = 1.796$ .

A plot of  $\log k$  against  $\sqrt{\mu}$  should give a result something



like that shown in Fig. 47. The relationship would no doubt hold very satisfactorily in extremely dilute solutions, and give an actual slope of  $+2$ . But difficulties intervene in following the course of the reaction with available analytical methods at such excessively small concentrations. Several encouraging results of this general sort have already been obtained by Brønsted and his students.

**REFERENCES:**

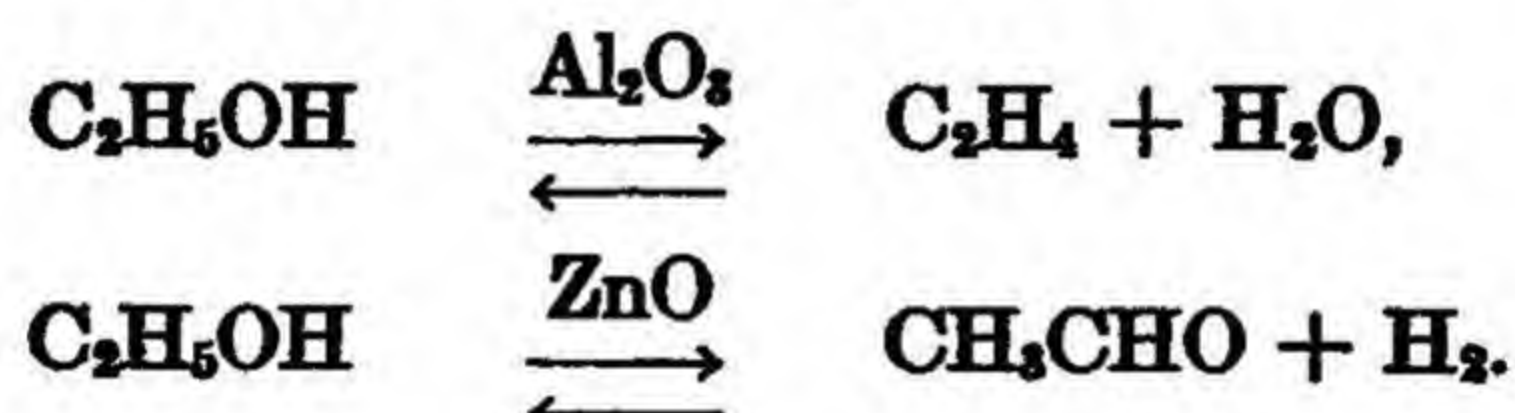
- Taylor, pp. 460-71, particularly good; also Taylor, Chap. VI.  
Rodebush, Chap. XIV.  
Getman and Daniels, Chap. XIV and pp. 477-80.  
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Brønsted, in Columbia Lecture Series, *Contemporary Developments in Chemistry*, Columbia Univ. Press; also *Chem. Rev.*, 5, 231 (1928).  
Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, Oxford Press.  
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## EXPERIMENT 27

### CATALYTIC DEHYDRATION AND DEHYDROGENATION OF ETHYL ALCOHOL

The specific catalytic characteristics of aluminum and zinc oxides in the simultaneous catalytic dehydration and dehydrogenation of ethyl alcohol has been demonstrated experimentally. The reactions taking place may be written as follows, where the selective influence of the catalyst is indicated:



The following simple experiment is designed to introduce the student to this type of work, to illustrate the specific influence of the catalyst and to indicate the influence of temperature upon the progress of the reaction.

#### EXPERIMENTAL

The apparatus is set up as shown in Fig. 48. A combustion furnace such as is used in organic combustions is most convenient, although a satisfactory electric resistance furnace may be made very easily. A layer of the catalyst is placed along the uniformly heated portion of the Pyrex glass tube, which may be about 1 cm. in diameter and 100 cm. in length; small wads of asbestos fiber may be used at the ends of the layer to keep it in position. One end of the furnace is raised a little so that the glass tube is in a slightly slanting position. The higher end of the tube is connected through a glass side-arm with the tube S, as shown. The top of tube S is closed by a one-hole rubber stopper carrying a short piece of glass tube drawn to a jet at its lower end and attached to the reservoir R by a length of rubber tubing. At the other end of the glass tube is attached a safety bottle B and a wash bottle W partly filled with water for collecting the condensed vapors of unchanged



alcohol and water and dissolving out the acetaldehyde. The delivery tube from the wash bottle is arranged so that it can be attached readily and quickly to a 100 cc. gas burette by a piece of rubber tubing.

When an experiment is in progress the furnace is kept at a constant temperature by regulating the resistance or by controlling the current supply, the temperature being read on a thermocouple pyrometer. The ethyl alcohol is fed slowly into the furnace by allowing mercury to flow from the reservoir R through the glass jet into tube S, which is filled with alcohol; the rate at which it is fed may be controlled by adjusting the height of the

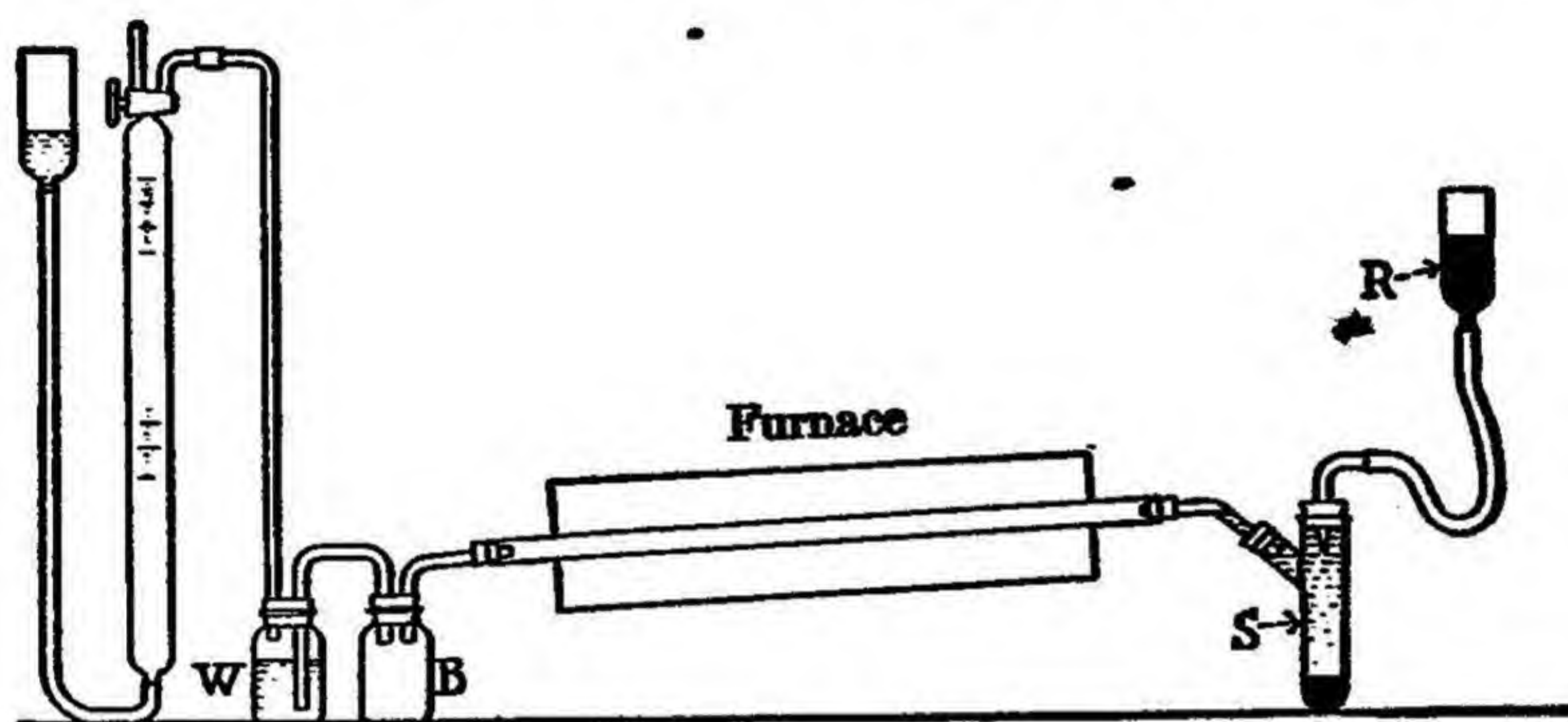


FIG. 48

reservoir and the size of the jet. After having allowed the reaction to proceed at a constant temperature for a few minutes a sample of the gas is collected in the gas burette by displacing a strong sodium chloride solution through which the gaseous products previously have been bubbled for some time.

The sample of gas is allowed to attain room temperature, is adjusted to a volume of 100 cc. at the barometric pressure, and is then analyzed by absorbing the ethylene with bromine water in a simple Hempel gas pipette. For the purpose of this experiment, other gases, such as carbon dioxide, which may be present, may be neglected. After thorough shaking with bromine water (if the bromine water becomes decolorized, a little liquid bromine should be added to the Hempel pipette) the residual gas is returned to the gas burette, allowed to attain room temperature again and the volume per cent of hydrogen is read off directly from the burette.



In this manner collect and analyze the products of the reaction at temperatures varying by steps of  $75^{\circ}$  or  $100^{\circ}$  in the range from  $200^{\circ}$  to  $800^{\circ}$  C. If desired, the products may be analyzed every  $50^{\circ}$  in the above given temperature range. Repeat with the other catalyst, using a new Pyrex tube.

Plot the volume per cent of ethylene against temperature, using the same sheet of co-ordinate paper for both cases. Which catalyst should be used in the commercial preparation of ethylene from ethyl alcohol by this process? What is the optimum temperature for the reaction?

As an additional study, the time required to collect 100 cc. of the gaseous products at the different temperatures should be noted, adjusting the rate of flow of ethyl alcohol to approximately the same value at each temperature. Plot the time required to collect 100 cc., against the temperature. At what temperature is the catalyst most efficient in promoting the reaction?

#### REFERENCES:

- Taylor, Chap. VI.
- Rodebush, Chap. XIV.
- Getman and Daniels, Chap. XIV.
- Millard, Chap. X.
- Findlay, Chaps. XII and XIII.
- Eucken, Jette and LaMer.
- Hinshelwood, *Kinetics of Chemical Change, etc.*
- Rideal and Taylor, *Catalysis in Theory and Practice.*
- Adkins *et al.*, *J. Am. Chem. Soc.*, 44, 385, 2175 (1922); 45, 809 (1923); 46, 130 (1924); 47, 807 (1925); etc.



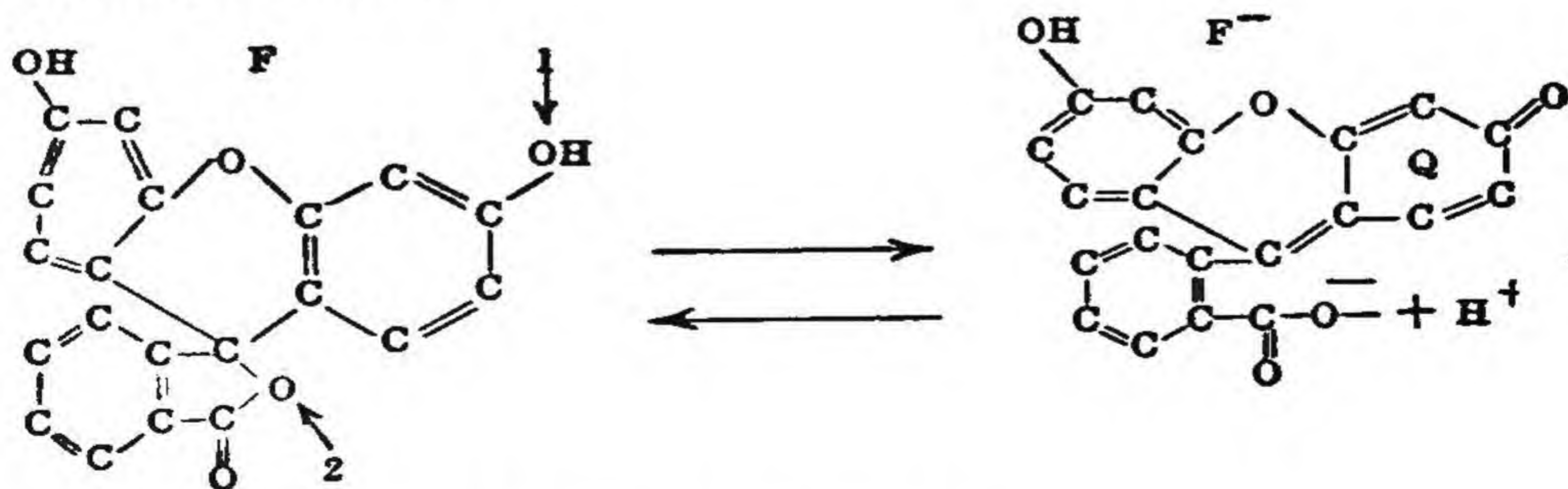
## EXPERIMENT 28

### QUENCHING OF FLUORESCENCE

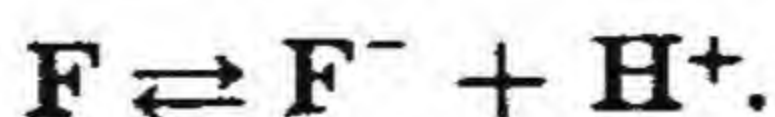
This experiment is designed to illustrate an interesting property possessed by certain ions of being able to quench fluorescence. The effect has been described in the literature by Perrin, *Ann. phys.*, [10], **12**, 169–275 (1929); *Comp. rend.*, **192**, 1727 (1931).

In a small agate mortar grind some fluorescein to a fine powder and weigh out 0.548 g. Dump it into a small beaker, add about 20 cc. water and 0.25 g. stick NaOH. Stir until all of the fluorescein, which forms a sodium salt with the NaOH, has dissolved. Pour into a liter volumetric flask and dilute to the mark, with distilled water. Since the molecular weight of fluorescein is about 332, a solution made up in this way will have its molecules evenly dispersed throughout the solution so that on the average there will be 1 fluorescein molecule for every little cube of volume  $10^{-6}$  cm. to an edge ( $10^{-13}$  cc.), or  $(100 \text{ \AA})^3$  or  $10^6 \text{ \AA}^3$ . One Ångström unit ( $\text{\AA}$ ) is  $10^{-8}$  cm. The student should check this calculation.

It will be observed that by transmitted light, shining *through* the solution, the color is red. But by reflected light, a beautiful greenish fluorescence shows itself. The theory of this effect is as follows. In structure, the molecule of fluorescein resembles that of phenolphthalein.



The two forms F and F<sup>-</sup> are in equilibrium





In form  $F$  the H-atom on oxygen atom 1 probably migrates to oxygen atom 2, and the  $\text{COOH}$  group thus formed ionizes to give  $\text{H}^+$ . In form  $F^-$  the quinoid grouping,  $Q$ , is present and this group is probably responsible for the color and the fluorescence. Upon addition of  $\text{NaOH}$ , the equilibrium is displaced to the right and the concentration of  $F^-$  increases. When these  $F^-$  molecules are irradiated with white light they absorb green light, and then the transmitted light, robbed of its green, shows the complementary color red. But soon after the molecules have absorbed the green light they emit it again, probably at a slightly longer wavelength, but still green. Such a re-emission is known as *fluorescence*. The fluorescent radiation is sent out in all directions, but is not observable in the transmitted beam because it is drowned out by the greater intensity of the red light.

Measure out 5 cc. of the fluorescein solution into each of 12 test tubes. Add 5 cc. of 1  $M$   $\text{NaCl}$  solution to the first test tube, 5 cc. of 1  $M$   $\text{NaNO}_3$  to the second, etc., etc., using also the following salt solutions: 1  $M$   $\text{Na}_2\text{SO}_4$ , 1  $M$   $\text{NaBr}$ , 1  $M$   $\text{NaI}$ , 1  $M$   $\text{KCl}$ , 1  $M$   $\text{KBr}$ , 1  $M$   $\text{KI}$ , 1  $M$   $\text{NaCNS}$ , 1  $M$   $\text{KCNS}$ , 1  $M$   $\text{NaCNO}$ , 1  $M$   $\text{KCNO}$ . It will be observed that in several of these cases the green fluorescence is quenched, and that the solution appears red even by reflected light. By a process of elimination it can be shown that the iodide ion,  $\text{I}^-$ , is by far the most powerful quenching agent in this list. If the student cares to, he may explore the quenching power of various other ions not mentioned here.

Now dilute, with distilled water, the solutions from which the fluorescence has been lost by the quenching, and note that the fluorescence reappears. Evidently, the quenching effect is a function of the concentration of the quenching ion. According to the theory, the fluorescein molecule  $F^-$  absorbs green light anyhow, whether or not any  $\text{I}^-$ , or other quenching ion, is present. But the absorbed energy is not immediately emitted. There is a small time lag. The absorbed energy sloshes around in the molecule for a small time interval before it finally becomes located in concentrated form in the particular group of atoms which serve as the emitting mechanism. If, during this time interval, an iodide ion, or other quenching ion, collides with the fluorescein molecule, the latter is robbed of at least a part of its accumulated energy, and it can then not emit at all, unless it again absorbs



more energy from the light. If the iodide ions are scattered more widely apart in the solution by dilution with water, there is a smaller chance that they will collide with the excited fluorescein molecules, and a better chance that the fluorescent emission will occur before collision.

It will be observed, in the large body of solution in the liter volumetric flask, that the fluorescence is much more intense in the part of the solution nearer the source of light, and on the far side, away from the light, the solution is practically red. This shows that all, or nearly all, of the green light has been absorbed from the incident beam before it completely traverses this depth of the solution; hence the fluorescein molecules on the far side are not excited, or only feebly excited, to fluoresce. The same effect can be demonstrated by filling two French square bottles, or other flat-side glass containers, with the fluorescein solution, and interposing one between the other and the light source. If the wavelength of the green light absorbed by a fluorescein molecule is  $5600 \text{ \AA}$ , let the student calculate the quantum of energy in ergs per molecule, and the total energy in calories absorbed per mol.

A very crude attempt may be made to estimate the magnitude of the time lag in the fluorescein molecule, as follows: Dissolve 27.4 g. KI in distilled water in a 100 cc. volumetric flask, and dilute to the mark. This will give a solution with one iodide ion,  $\text{I}^-$ , in every  $(10 \text{ \AA})^3$  or in every  $10^{-21}$  cc. of volume. Run this solution from a burette into 10 cc. of the fluorescein solution, until almost complete quenching has occurred. The addition of 1 cc. of the KI solution will make a noticeable difference, but about 10 cc. will be required to make the quenching practically 100%. The volume of the mixed solutions is now 20 cc., which means that there is one  $\text{I}^-$ , on the average, in every  $2 \times (10 \text{ \AA})^3$  of volume, and one fluorescein molecule in every  $2 \times (100 \text{ \AA})^3$  of solution volume. The situation may be idealized somewhat and represented as in Fig. 49. Let us suppose that the iodide ions are distributed in a cubic net, and are located at the corners of cube volumes of  $2 \times (10 \text{ \AA})^3$ . Such cubes have edges  $12.6 \text{ \AA}$  in length. The iodide ion has a radius of  $2.2 \text{ \AA}$ . Now, the fluorescein molecule which is located somewhere within a much larger cube,  $2 \times (100 \text{ \AA})^3$ , may be considered at any particular instant



as being centered in one of the smaller iodide cubes, since all of these are alike, and it does not make any difference in our argument in which particular one the fluorescein molecule happens to be. While the fluorescein molecule is certainly not a sphere, we may suppose, for the sake of simplification, that it behaves as such on the average, as far as collision

with  $I^-$  is concerned. Such a fluorescein molecule sphere would probably have a diameter of about  $12 \text{ \AA}$ . Thus along a cube diagonal, from corner to corner, a distance of  $21.8 \text{ \AA}$  ( $\sqrt{3} \cdot 12.6 \text{ \AA}$ ), the distance between the surface of an iodide ion and the surface of the fluorescein molecule would be about  $2.7 \text{ \AA}$ . If we assume that this is the arrangement of the parti-

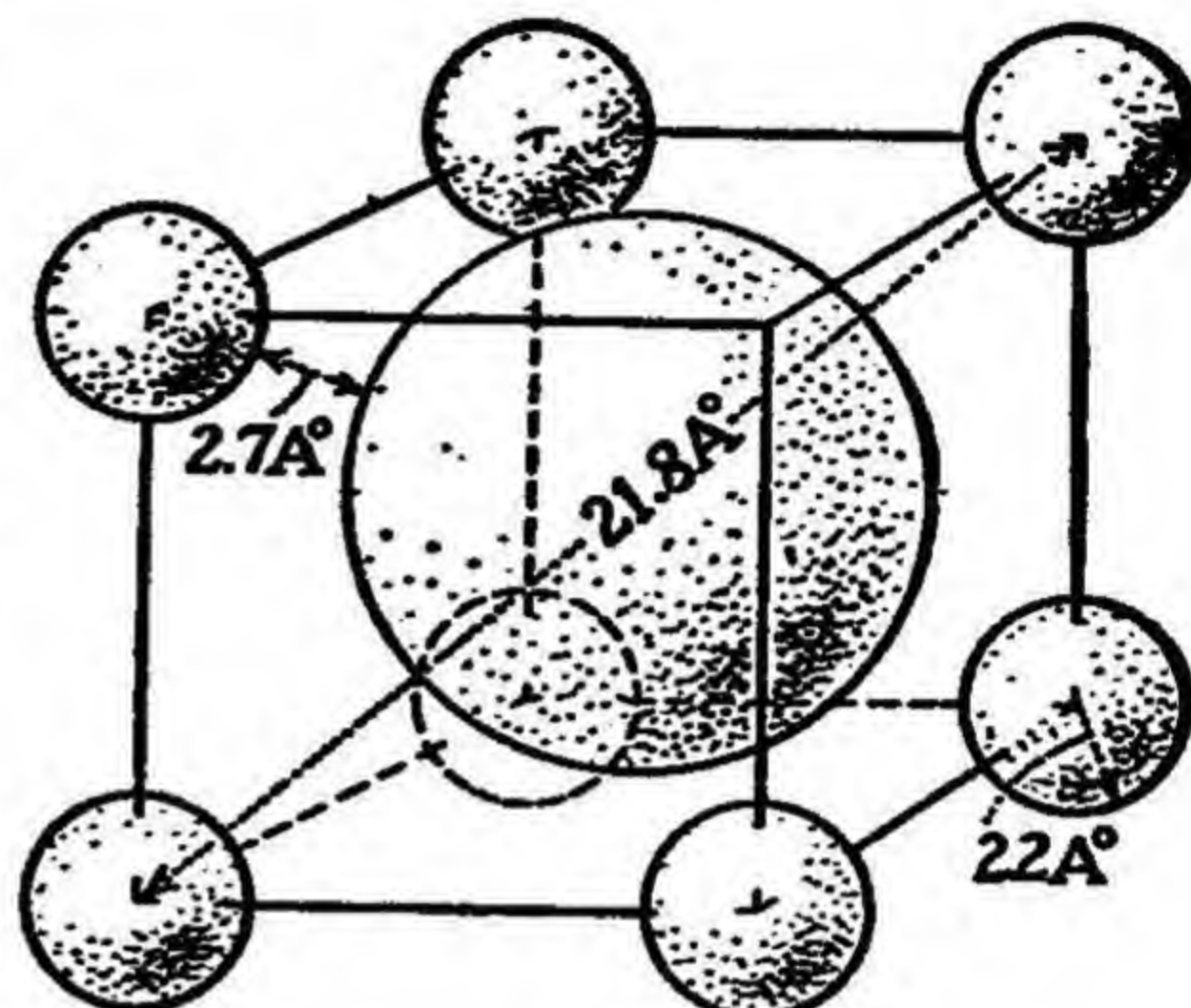


FIG. 49

cles at the instant that the fluorescein molecule absorbs the green light, and if we assume that at least one of the eight iodide ions will move toward the fluorescein molecule, the distance to be travelled, on the average, to make impact, would be  $2.7 \text{ \AA}$ . Since in a liquid the mean free path is of the same order of magnitude as the particle diameter, we would not be making a large error in assuming that the iodide ion would travel this short distance at about the same velocity as would a gaseous

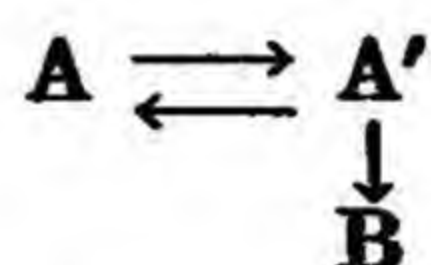
ion, namely,  $u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.32 \times 10^7 \times 300}{127}} = 2.4 \times 10^4 \text{ cm./sec.} = 2.4 \times 10^{12} \text{ \AA/sec.}$  Therefore it would take the  $I^-$  about  $10^{-12}$  seconds to reach the fluorescein molecule. Assuming further that theft of the absorbed energy occurs instantly on impact, and that every collision is *effective*, i.e., that the  $I^-$  is not required to hit the fluorescein molecule at some particular spot on its surface, but can de-activate it by striking it anywhere, the time lag between absorption and emission of fluorescence would be about  $10^{-12}$  seconds.

We have made a lot of assumptions here, some explicitly expressed and other implicit ones, and we would be very fortunate indeed if our guess of  $10^{-12}$  seconds is not off by ten thousand



times. It might well be  $10^{-8}$  seconds. At any rate it seems likely that the lag is an extremely short interval of time.

This lag between absorption and emission of energy, which probably accounts for the quenching effect we have been observing here, is a helpful illustration of a point which has attained considerable importance in recent theory of uni-molecular reactions. There has been a difficulty in accounting for the velocity of uni-molecular gas reactions. If the energy of activation of the molecules, which conditions them for chemical reaction (see Exp. 26), be supposed to come from collisions between molecules, the chemical velocity should be proportional to the square of the pressure, since the number of collisions per unit time is proportional to the square of the pressure. The facts are quite otherwise. The velocity is independent of pressure, over a long range. In an effort to resolve the difficulty, the "radiation theory" was suggested, according to which the molecules get their energy of activation by absorption of infra-red, heat, radiation. This theory had to be discarded because of its many manifest difficulties and absurdities. Some years ago Lindemann proposed an interesting mechanism. A small fraction



of the normal molecules A change into activated molecules A', rich in energy, by collision (shown by arrow to right) and A' molecules then react to form the product molecules B. But the energy-rich molecules A' do not react immediately upon picking up their extra load of energy. This energy is supposed to wander around within the molecule for a short "lag" time, before it becomes properly concentrated and located at the most fragile spot in the molecule and then causes fracture (a lag very much like that in the fluorescein molecule before emission of fluorescence). In the meantime the A' molecule may be struck by an unactivated molecule A and robbed of its energy, before chemical reaction can take place. The de-activation process, changing of A' back to A, is represented by the arrow to the left. This theft of the activation energy by collision is almost as rapid as the formation of activated A' molecules. The concentration of A' molecules which escape de-activation during the lag is small. This concentration



is independent of pressure; and this concentration determines the rate of formation of B, and hence the rate of the chemical reaction.

Lindemann's mechanism is plausible in many ways. In favor of it, we may say here in our present setting that only *fairly complicated* molecules are found to undergo uni-molecular reaction. This is probably because only in complicated molecules would there be a time lag, a time for the acquired energy to slosh around and be momentarily lost among the various bonds of the molecule. No uni-molecular *gas* reactions would probably ever involve molecules, however, as complicated in structure as fluorescein.

REFERENCES:

- Taylor, Chap. XIV.
- Rodebush, Chaps. XIV and XVII.
- Getman and Daniels, Chap. XX.
- Millard, Chap. XI.
- Findlay, Chap. XVII.
- Eucken, Jette and LaMer.
- Rideal and Taylor, *Catalysis in Theory and Practice*.
- Ruark and Urey, *Atoms, Molecules and Quanta*, McGraw-Hill.



## EXPERIMENT 29

### THERMIONIC TUBES

A three electrode thermionic or radio tube such as the UX-201-A type, or UX-301-A or any of the usual radio tubes is selected for the present experiment. Disregard for the moment the grid G, and consider the filament F and plate P in Fig. 50. If the tungsten filament of this tube is heated with a current, from battery aB,

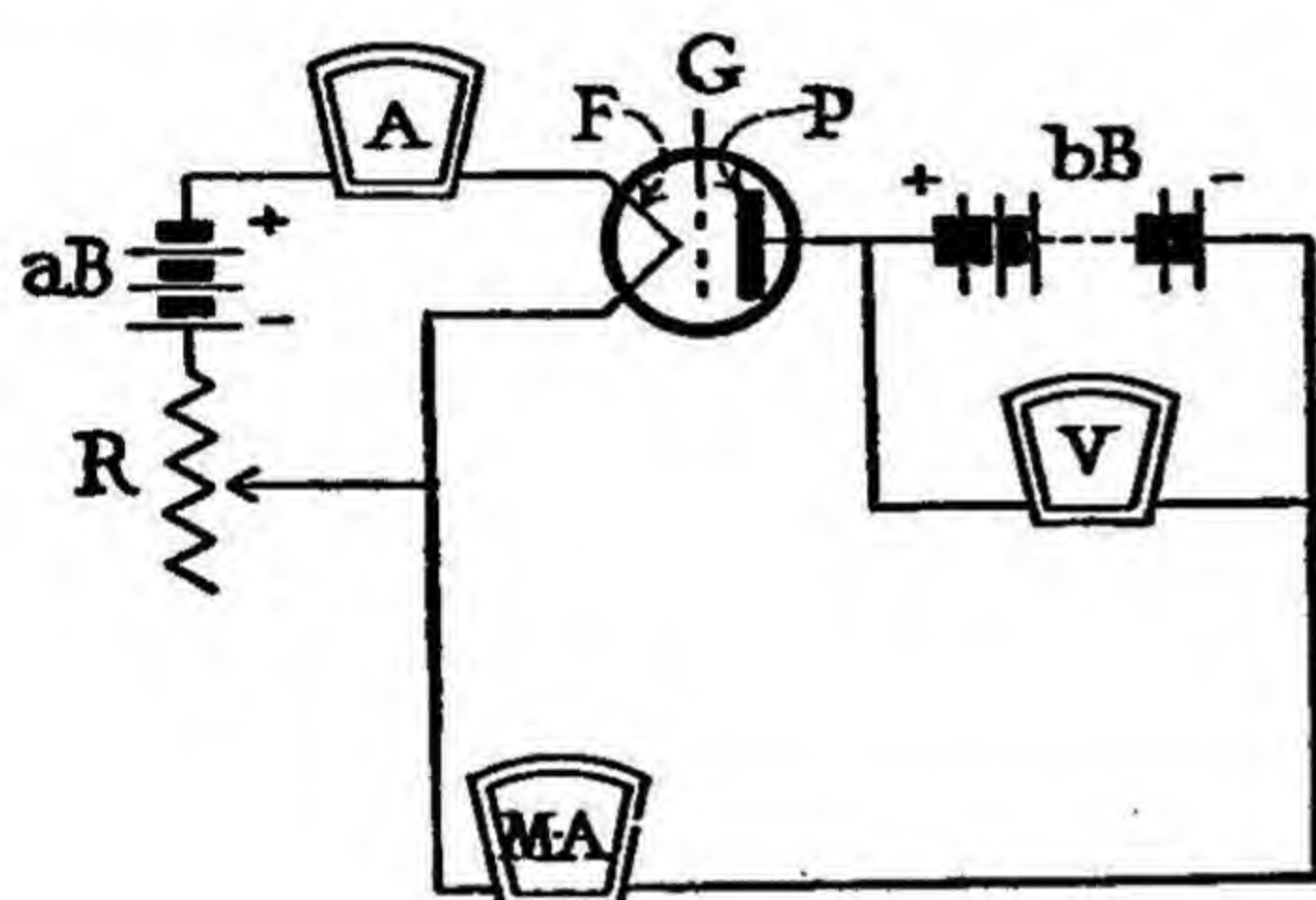


FIG. 50

free electrons escape from it into the vacuum at a temperature far lower than that required to volatilize appreciably any of the metal itself. When the electrons escape they leave a positive charge on the hot filament. The negatively-charged cloud of electrons, or "space charge" as it is sometimes called, is held more or less

closely in the neighborhood of the filament by electrostatic attraction. The equilibrium thus established resembles in many respects the equilibrium between a saturated vapor and a hot liquid or solid, and in a certain sense we may speak of the "electron vapor pressure." If the negative pole of another battery, bB, is connected to the hot filament and the positive pole to the plate P, the cloud of electrons will be repelled from the filament, which is now negatively charged, and will be attracted by the positively charged plate; and while the electrons are leaving the neighborhood of the hot wire, other electrons are boiled out, and hence a continuous stream passes across the vacuous space of the tube from filament to plate, and also through the circuit PbMAFP. Such a streaming of electrons constitutes an electric current. (In the conventional nomenclature, however, the current is said to flow in the opposite direction.) The strength of



this "plate-current," as it is sometimes called, is indicated on the milli-ammeter M.A.

Such a thermionic tube may be used to rectify an alternating current, by connecting one lead wire from the generator to the hot filament and the other to the plate. When the *filament* is charged negatively, an electron current flows through the tube from the hot filament to the plate, but when the *plate* becomes negatively charged, no current passes in the opposite direction since the plate is not heated and does not emit electrons.

#### EXPERIMENTAL

(A) The ability of the tube to rectify an alternating current may be demonstrated with the apparatus shown in Fig. 51. First turn the two-way switch S

to contact C, and by letting the 110-volt 60-cycle a.c. current, with the electric light bulb L in series, flow through the dilute potassium iodide-starch solution in the beaker B, show that iodine is liberated at both platinum wire electrodes. Then, using a 5-6 volt storage battery aB, a variable resistance R and the ammeter A, heat the filament

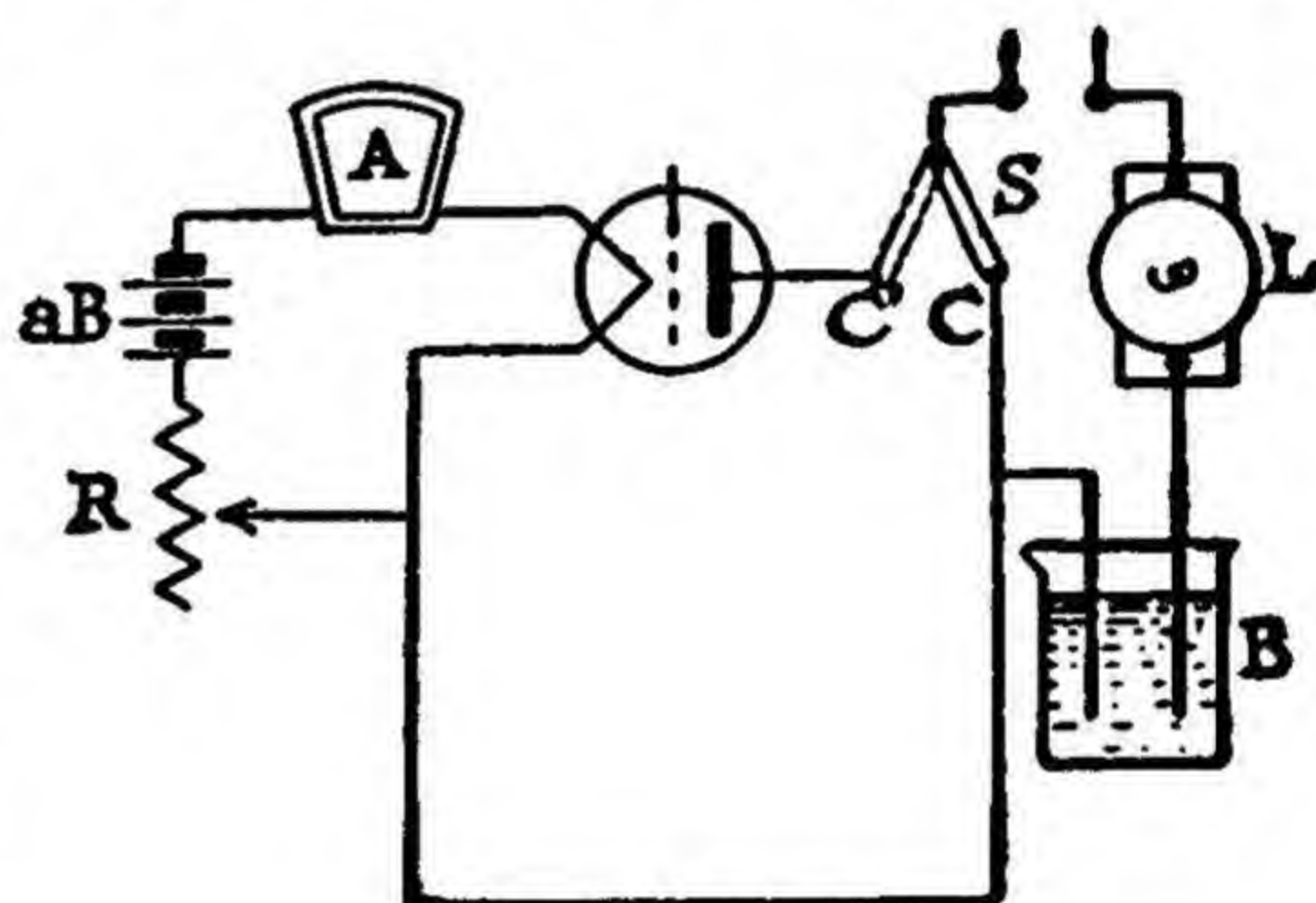


FIG. 51

aB, a variable resistance R and the ammeter A, heat the filament with a current of 0.25 ampere. It is not advisable to send a stronger current than this through the filament due to the danger of burning it out, or at least of shortening its life. There will be found on the paper box in which the tube is purchased, or on the manufacturer's direction sheet accompanying the tube, a statement of the maximum filament heating current. Throw the switch S to contact C', and note that iodine is now liberated from only one electrode. The iodine identifies the positive electrode.

The rectified current is unidirectional but intermittent, not continuous. By employing two tubes, one operating a half wave length out of phase with the other, it is possible to superimpose two intermittent currents, and obtain a continuous direct current from an alternating current. There is one condition under which a



thermionic tube will conduct the current in both directions, and hence lose its ability to rectify, namely the condition that arises when the plate is heated by bombardment of the filament electrons to a point where it also emits electrons. Such a situation is produced when the plate voltage is high, and when the kinetic energy of the electrons is relatively large as they strike the plate, due to their acceleration through the electrostatic field.

Assuming that there is a potential difference between the filament and plate of 100 volts, calculate the kinetic energy of a single electron at the moment of collision with the plate, using the equation

$$Ve = \frac{mv^2}{2}$$

where  $V$  is the voltage, and  $e$ ,  $m$  and  $v$  are respectively the charge, mass and velocity of the electron. Remember that a volt is equal to  $10^8$  electromagnetic units of potential and that the charge on an electron in electromagnetic units is  $1.59 \times 10^{-20}$ . Calculate the velocity with which an average electron starting from a position of rest at the filament will strike the plate. Calculate the heat produced on impact, assuming that all of the kinetic energy is changed into heat. How many electron impacts of this sort would be required to bring a tungsten plate 1 g. in weight to a red heat ( $580^\circ \text{C.}$ ), if none of the heat is lost by radiation or conduction, and if the specific heat of tungsten is taken as being constant at 0.034? How long a time would be required to produce this result if a "plate current" of 2 milli-amperes were flowing?

(B) Arrange the apparatus as shown in Fig. 50, and heat the filament with a current of 0.25 ampere. Connect the positive end of a battery bB (which may consist of a series of dry batteries or of the usual "B-batteries" or which may be replaced by a B-battery eliminator) to the plate and the negative end to the filament. Measure on the milli-ammeter M.A., and record, the successive plate currents when the voltage on the plate is altered in steps of 10 volts (or other convenient intervals) starting with zero, and increasing it finally to about 135 volts, or high enough so that there is no further increase in plate current with increasing plate potential. A milli-ammeter with a range of 0-15 milli-amperes and with a scale which can be estimated to 0.01 milli-



ampere, should be employed. It may be necessary to heat the filament for a short while in order to obtain concordant readings. Now cut down the filament heating current by 0.02 ampere, and again note the plate currents at various plate voltages. Continue taking sets of readings at successively lower filament currents, until the plate current at the highest plate voltage drops off to 0.05–0.10 milli-ampere.

Plot the plate current (ordinate) against plate voltage, making a separate curve for each value of the filament current, but plotting them all on one piece of paper. The flat portions of the curves correspond to the "saturation currents." At each filament temperature, a sufficiently high plate voltage may be finally reached, at which practically all of the electrons being emitted from the hot filament are drawn over to the plate, and when this voltage is imposed on the plate the electron current cannot be materially increased even with much higher plate potentials. The saturation current at each temperature is thus a measure of the number of electrons given off by the filament at that temperature. The saturation current  $I$  as a function of filament temperature is given by the Richardson-Dushman equation

$$I = A \cdot T^2 \cdot e^{-\frac{w_0}{kT}} = A \cdot T^2 \cdot e^{-\frac{b}{T}}$$

where  $A$  and  $b$  are constants characteristic of the substance of which the filament is made,  $k$  is the Boltzmann gas constant, and  $w_0$  is the work required to remove one electron from the filament at the absolute zero. Here again we meet the Boltzmann factor. (See Exercise III.) In the present experiment we shall not be able to determine the temperature of the filament, and hence we cannot test here the validity of this equation. The student will find a profitable discussion of this equation, giving latent heat of evaporation of electrons from the filament, in Langmuir's most interesting Chandler Lecture, *J. Ind. Eng. Chem.*, 22, 390 (1930).

Now plot the measured plate currents against filament heating current, making a separate curve for each value of the plate voltage. Note that here again the curves flatten out. When the plate voltage is held at a constant value, and the filament heating current gradually increased, the cloud of electrons emitted by the filament grows to such an extent that the negative charge or



"space charge" thus accumulated about the filament is large enough to exert a repellent effect on the other electrons being emitted, and balance off some of the attractive pull of the plate. When this equilibrium state is reached, the plate current will not increase with rising filament temperature. To increase the current, the plate voltage must be raised. Langmuir (*Gen. Elect. Rev.*, p. 330, 1915) has shown that the plate current  $I$  (in amperes) corresponding to the flat portions of the curves is related to the plate potential  $V$  (in volts) as follows:

$$I = aV^{\frac{3}{2}}$$

where  $a$  is a constant. Test the validity of this equation by substitution of your data therein, and thus determine whether  $a$  is a constant.

(C) Arrange the circuit as indicated in Fig. 52. Heat the filament with a current of 0.25 ampere. Make the plate voltage

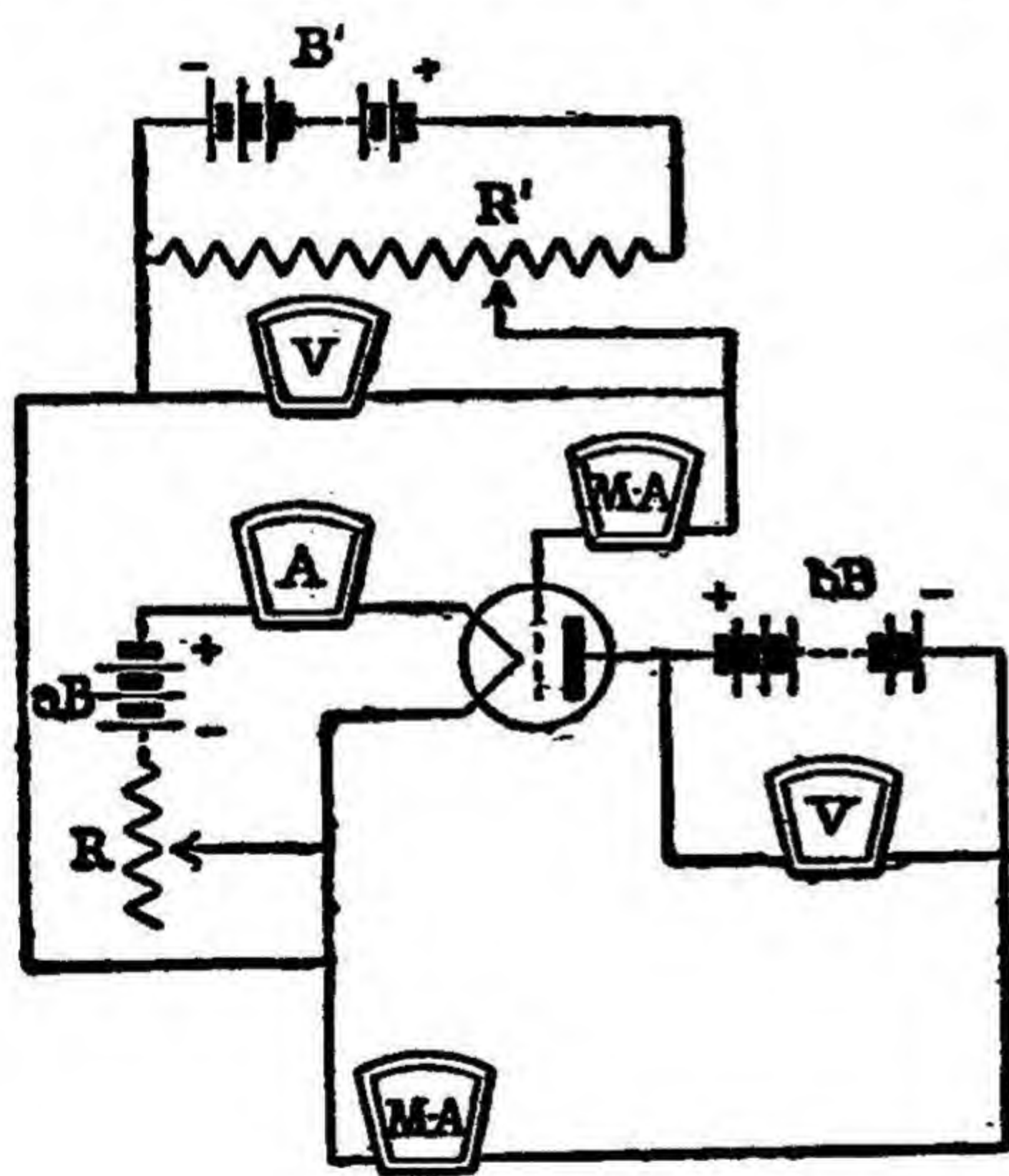


FIG. 52

about 10. By means of the battery  $B'$  and the rheostat  $R'$  impose such a negative potential on the grid  $G$  with respect to the filament (the poles of battery  $B'$  will have to be the reverse of those shown in the figure) that no plate current flows. In several successive steps bring the grid potential to zero, and note that there is no grid current as measured by the milli-ammeter in the grid circuit, although the plate current increases. Then reverse the polarity of battery  $B'$ , and make the

grid  $G$  gradually more and more positive with respect to the filament in steps of 1–2 volts, until a value of 15–20 volts has been attained, noting the grid potential, the grid current, and the plate current.

Plot plate current against grid potential. What is the relative



effect of change in the grid potential and in the plate potential on the plate current? The positive charge imposed on the grid has the effect of neutralizing some of the space charge, and by raising the grid potential high enough the plate current can be increased up to the saturation value characteristic of the filament temperature. On this same paper plot grid current against grid potential. Observe that the flow of a small grid current is able to control the flow of a relatively large plate current. It is on this relationship that the amplifying action of a thermionic tube depends. If desired, the plate voltage may now be increased in steps of 30–45 volts and the effect of grid potential on plate current determined as before.

After performing this experiment the student should read Langmuir's account of studies of adsorption made with the help of measurements of thermionic emissions (pp. 2270–82 of a paper in *J. Am. Chem. Soc.*, 38 (1916)). For a general discussion of the theory of the properties of thermionic tubes, the student is referred to the following books:

Van Der Bijl, *Thermionic Vacuum Tube*.

Lauer and Brown, *Radio Engineering Principles*.

Crowther, *Ions, Electrons and Ionizing Radiations*.

Chaffee, *Theory of Thermionic Vacuum Tubes*, McGraw-Hill.

Dushman, *High Vacuum*.

Hoag, *Electron Physics*.

Starling, *Electricity and Magnetism*.



## EXPERIMENT 30

### DIELECTRIC CONSTANT OF LIQUIDS

The dielectric constant or specific inductive capacity of a substance may be defined as the ratio of the capacity of a condenser with and without the substance between the plates. The dielectric constant of air for ordinary purposes may be taken as unity. If then, one has a means of comparing the capacity of a condenser with some substance between its plates with its capacity when air is used as a dielectric, the dielectric constant of the substance may be easily calculated.

In Fig. 53 if the condenser AB, charged with a battery, is allowed to discharge through the coil L, electrons from the negatively charged plate A will flow through L onto the plate B. The current of electrons does not stop flowing when A and B have reached the condition of equal potential (no charge); for, when

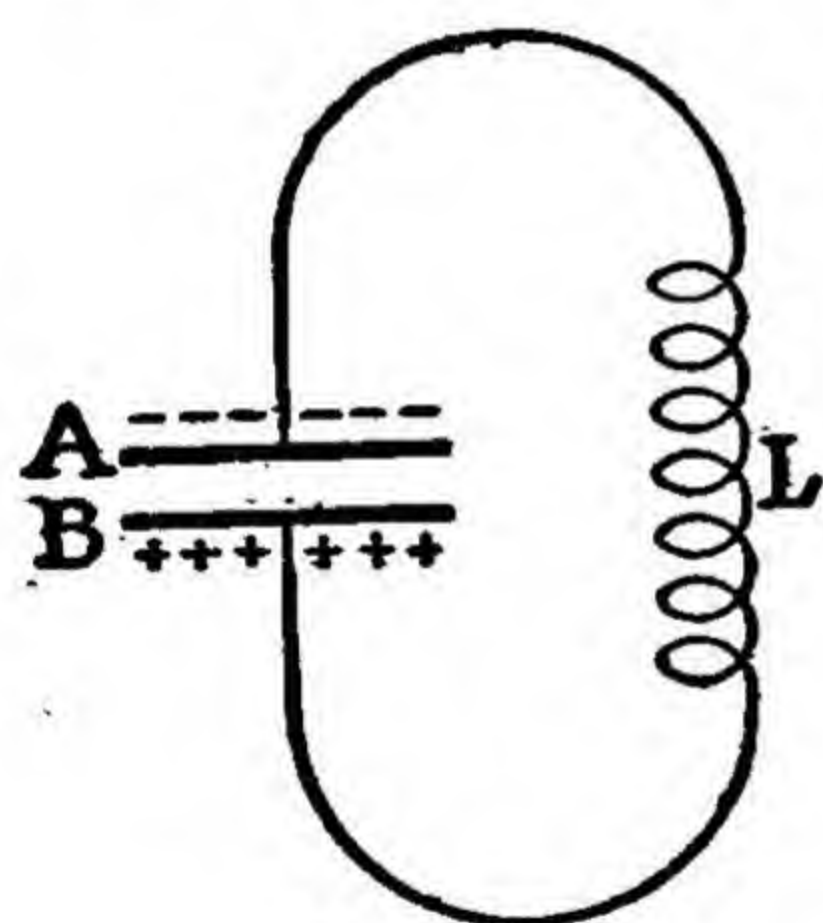


FIG. 53

the stream of electrons begins to slow up as a result of falling potential difference between A and B, the electromagnetic field generated in L tends to keep it in motion, and as a consequence, plate A continues to lose electrons and becomes positively charged, and plate B assumes a negative charge. Discharge then occurs in the opposite direction, and the electrons keep swinging back and forth through the circuit from plate to plate, very much like a moving

pendulum, until the electrical energy is dissipated as heat in overcoming the resistance of the circuit. The frequency of this oscillation depends upon the capacity of the condenser and the inductance of coil L, as shown by the equation

$$n = 1/(2 \pi \sqrt{L \times C}) \quad (1)$$

where  $n$  is the frequency,  $L$  the inductance (henrys) and  $C$  the capacity (farads). This holds true when the resistance of the



circuit is small, as is generally the case. For derivation of this equation and details of its application, the student is referred to modern texts on electricity and magnetism, or the books listed at the end of these directions. The student should prove the dimensional homogeneity of this equation (see Exercise I).

In the present experiment an oscillating circuit of this sort is set up, and a radio tube is employed to amplify the oscillating current and feed it back into the circuit so that the oscillating current does not fall off finally to zero, but is maintained. The capacity and inductance of the oscillating circuit are adjusted so that the observer is able to tell when the capacity in the oscillating circuit is at a certain value; that is to say, the condenser is adjusted so that the oscillating circuit is "tuned" to a "wave meter" also consisting of a condenser and an inductance coupled to the inductance in the oscillating circuit, a pair of telephones being employed to test for this tuned condition. The condenser in the oscillating circuit (this is better called the sending circuit) is really made up of two condensers in parallel. One of these condensers has its plates immersed in the substance whose dielectric constant is to be determined. By noting the change that must be made in the capacity of the other condenser in order to keep the sending circuit in tune with the receiving circuit, when air and the substance under investigation are used successively as dielectrics in the first condenser, it is possible to find the ratio between the two capacities, and hence the dielectric constant.

#### EXPERIMENTAL

Construct the oscillating (Hartley) and wave meter receiving circuits indicated in Fig. 54. It is perhaps advisable to have the various pieces of apparatus fastened in place to a baseboard, and equipped with binding posts, so that the student may make the necessary wiring and connections. The tuner or radio-frequency transformer  $L$  is an ordinary vario-coupler. A Birnbach tuning unit may be used, in which case the small primary coil on the stator is neglected. The stator coil is tapped approximately in the middle, for the Hartley oscillation circuit, and the rotor is used in the receiving circuit. The radio tube may be of the UX-201-A type or UX-301-A.

The variable condenser  $C_0$  must be of the "straight capacity



line" type, in which the plates are semi-circular and the axis of rotation passes through their center of curvature. It is preferable to use two such standard condensers, which may be permanently connected in parallel, of about 0.0005 and 0.0001 mfd. capacity, as the smaller condenser may be used when liquids of low dielectric constant are examined and the larger one for liquids of somewhat higher dielectric constants. (Experimentally, it has been found

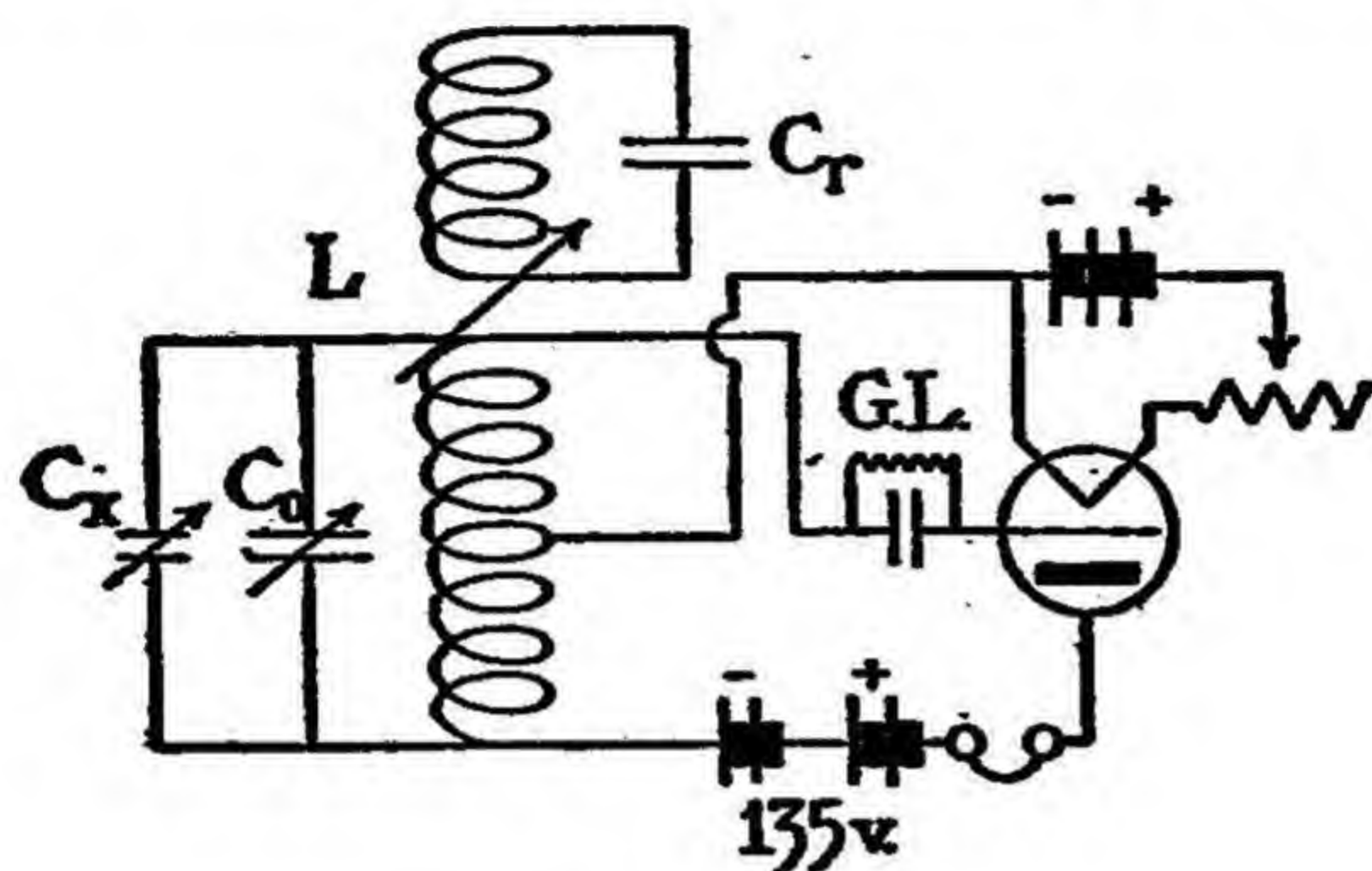


FIG. 54

that the method and apparatus described here are suited for liquids of low specific inductive capacity, say below 10. The dielectric constant of nitrobenzene, which is almost four times as great as this figure, may be found fairly accurately, but those of liquids like acetone,  $K = 20.5$ , are very erratic, or one may be unable to determine them at all.) It is immaterial how the dials for these condensers are marked; the usual type has a scale from 0 to 100 through an angle of  $180^\circ$ .

The student should calibrate one standard condenser in terms of the other so that he may use the smaller one when air is the dielectric and the larger when a liquid is used; this is done by setting one condenser at two different points and tuning with the other until the total capacity is the same in each case. The differences in the readings of the two condensers then represent the same capacity; thus one gets a factor by means of which a capacity measured with one condenser can be converted to the units used on the other. This procedure enables one to measure the dielectric constant of almost all of the liquids mentioned below to three significant figures.



The experimental condenser  $C_x$  is connected in parallel with  $C_0$  and may consist of a small balancing condenser (about 0.00005 mfd.), preferably gold-plated. For getting the dielectric constant of nitrobenzene it may be necessary to use a condenser of this type from which all the plates have been removed except two stator plates and one rotor plate, spaced fairly far apart. The condenser  $C_r$  in the receiving circuit may be a fixed condenser of about 0.005 mfd. The grid condenser and the grid leak, G.L., in the oscillating circuit may be variable or may have the values 0.00025 mfd., and 10 meg., respectively. It is best to have available several grid leaks, varying from 0.1 to 10 meg., and to determine by trial which one gives the most satisfactory results.

The values given above for the condensers are those that have been found to give very satisfactory results. Other values may, however, be used. In fact it is advisable to experimentally determine what values give the best results. The condenser  $C_r$  should have such a capacity as will bring the reference point (see below) well up on the scale of  $C_0$ . Thus, if  $C_0 = 0.001$  mfd., then  $C_r$  may be 0.008 mfd. This reference point should not, however, be brought too close to the ends of the scale as the capacity of  $C_0$  does not follow a straight line near the ends of the scale.

The filament of the tube may be heated by a 6-volt storage battery, the current being regulated by means of a 30-ohm rheostat. It is, however, much more convenient to make use of the a.c. electric light current, stepping it down to 5–8 volts with a toy transformer, as the additional hum is not objectionable. The filament current should be kept as low as is consistent with good operation. The B-battery in the oscillating circuit may have an electromotive force of 90 volts; but one of 135 volts is better. It may be very conveniently replaced by a B-battery eliminator. Lower voltages may be found to work, but not as well as those suggested. For very accurate work the coils and condensers should be shielded by being enclosed in a box lined on all sides with sheet iron (which is grounded). This will eliminate the influence of the capacity of the operator's body and also any possibility of radiation to neighboring radio receivers. No ground except that for the sheet iron shield need be provided, although if desired the negative end of the filament may also be grounded. In this experiment, however, no shielding will be necessary if the



student takes all readings with body and hands in the same position for each reading.

To determine the dielectric constant of a liquid the inductive coupling  $L$  and the capacity  $C_0$  are varied until sharp tuning is achieved. Or, one may tune to some nearby broadcasting station of known wave-length. As one varies the capacity of  $C_0$  in both directions clicks are heard in the telephones when the wave meter falls into resonance with the sending circuit; at these points the wave meter absorbs so much energy that the sending circuit stops oscillating at the frequency characteristic of the wave meter. The region between the two clicks may be made very narrow by loosening the coupling between the two inductance coils and its midpoint is taken as the "null" or reference point. Four readings of  $C_0$  are now taken: (1) when the rotor plates of  $C_x$  are "out," using air; (2) when they are "in"; (3) when they are "out," using the liquid as dielectric and (4) when they are "in." The difference between (1) and (2) gives a measure of the capacity of  $C_x$  when air is the dielectric; that between (3) and (4) gives a measure of its capacity when the liquid is the dielectric. This differential method is used to permit the permanent connection of  $C_x$  and  $C_0$  and to eliminate the effect of the leads from  $C_x$ . By dividing the second difference by the first the dielectric constant of the liquid is found.

Determine the dielectric constant of the following liquids: benzene, toluene, xylene, brombenzene, chlorbenzene, aniline, nitrobenzene, ether, chloroform, carbon tetrachloride. Compare with the values given in tables. If desired the dielectric constant of acetic acid may be compared with that of chlor-acetic acid by adding 1/30 mol of each to separate 50 cc. portions of benzene, and making the tests with these solutions.

Calculate, with Equation 1, the approximate frequency which is absorbed by the wave meter. Since air is used in the case of the coil the inductance may be calculated by the equation  $L = 4\pi^2 n^2 r^2 s$ , where  $L$  is the inductance in centimeters,  $n$  is the number of turns of wire in one centimeter length,  $r$  is the radius of the coil in centimeters and  $s$  is the length of the coil in centimeters.

How many c.g.s. units are there in one henry?

**Electric Moments.** The charge which the condenser can be made to hold, in other words, the magnitude of the dielectric constant of the substance between the condenser plates, depends



on two quite distinct and separate effects. (1) First, it depends on the *induced polarity*, which means the polarization or separation of  $-$  and  $+$  charges within the molecules (of the substance between the condenser plates) which is produced when the electrical field is on. This *induced polarity* is not present normally, but in the electrostatic field of the condenser, electrons within the molecules are torn out of their usual positions and are displaced or shifted with respect to the positively charged atom nuclei in the molecules. Such an induced separation of intra-molecular charges will of course neutralize to some extent, by induction, the charges on the condenser plates, and hence increase the capacity of the condenser. (2) In the second place, the molecules may be *permanently* polarized, i.e., there may be a permanent separation of negative and positive electricity, due to the nature of the molecule's structure. Then, Fig. 55, when the plates are charged, an orientation or setting of the molecules in one direction will be produced, with the positive ends pointing toward the negative plate, and the negative ends toward the positive plate. With the positive ends pointing one way, some of the negative charge on the plate will be neutralized by induction; and the same will be true of the positive charge on the other plate. Hence, with a given impressed potential difference, a larger quantity of charge can be run onto the plates. It should thus be evident that the capacity of the condenser will be greater the larger the electric moments of the molecules, that is, the greater the separation of positive and negative electricity within the molecule and the greater the size of the charge separated.

If the temperature is raised higher and higher the increased thermal agitation, which tends to give a purely chaotic arrangement of the molecules, cuts down the magnitude of the effect produced by the *permanent* polarization, but does not disturb appreciably the induced polarization. Debye has developed the theory of the permanent polarization, and indeed it is possible to untangle the two effects, by measuring the dielectric constant

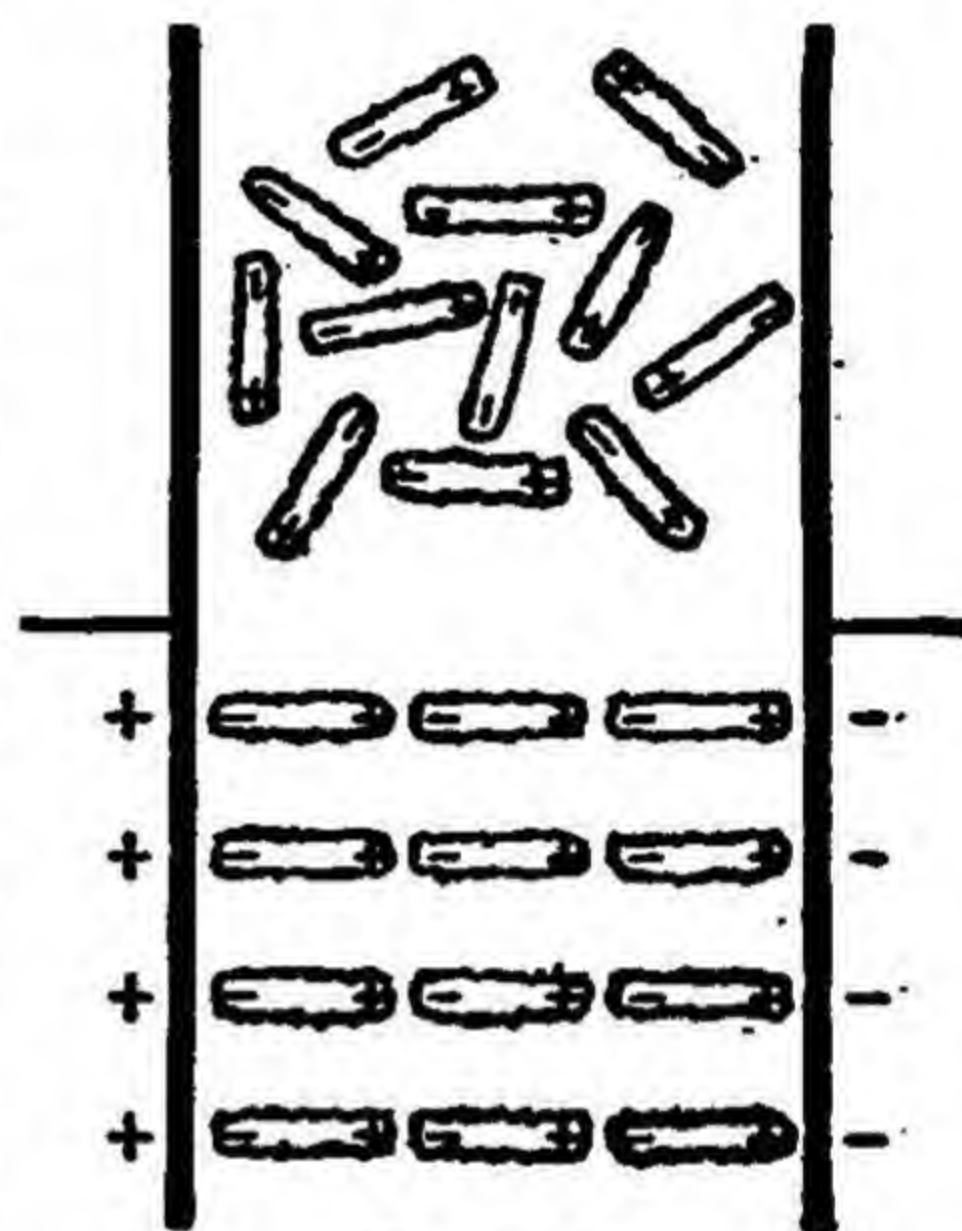
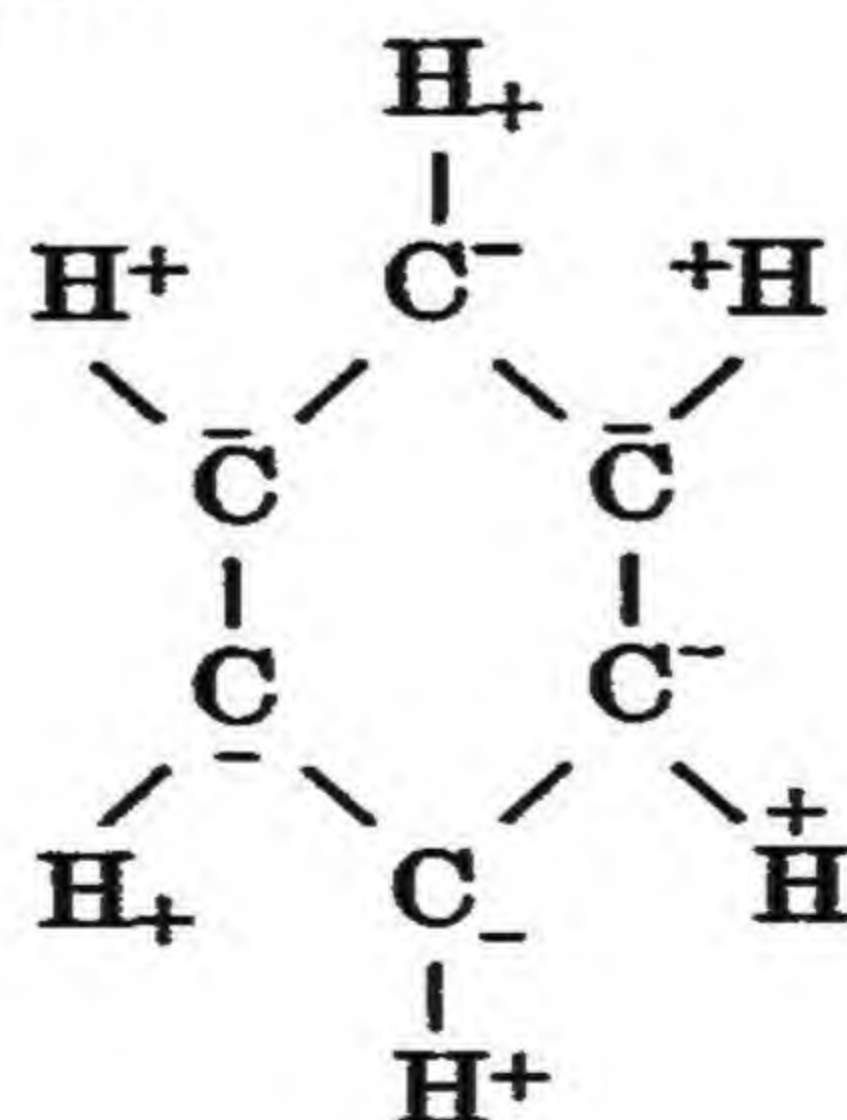


FIG. 55



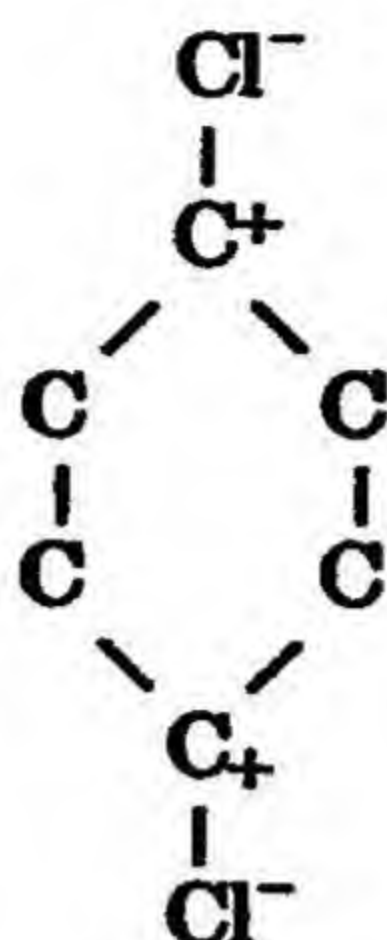
at a series of different temperatures. Out of such a treatment we can get what is known as the permanent *electric moment* of a molecule. If the permanent separation of charges within a molecule, due to the nature of the constituent atoms and their spacial arrangement with respect to one another, is represented as follows,  $+\text{-----}-$ , the electric moment is defined as the product of the distance of separation (measured in cm.) and the charge, either  $+$  or  $-$  (measured in electrostatic units),  $m = e \cdot l$ . Since the calculated electric moment, in these units, varies all the way from zero, for those molecules which do not possess any permanent separation of charges, up to about  $6 \times 10^{-18}$ , and since the charge on an electron is  $4.77 \times 10^{-10}$  e.s.u., it is obvious that the actual distance of separation of  $+$  and  $-$  charges in molecules which have so far been studied would vary from zero up to a little more than  $1 \times 10^{-8}$  cm., i.e., to a little more than 1 Å (Ångström unit).

The permanent electric moment of a molecule is a very significant quantity. If we know its magnitude we can often make very important deductions regarding the structure of the molecule. For example, in spite of the fact that the dielectric constant of benzene ( $\text{C}_6\text{H}_6$ ) is about 2.2, it can be demonstrated that all of this arises from the *induced* polarization; benzene has no permanent electric moment. This is what we would expect from our theory of benzene ring structure. Even if there is a permanent moment at every C—H bond, thus



the symmetry of the arrangement would cause the moments to balance out. On the other hand in chloro-benzene there is a permanent moment,  $1.5 \times 10^{-18}$ , at the C—Cl bond. Now in para-dichloro-benzene





the two oppositely directed moments (each  $1.5 \times 10^{-18}$  cm. e.s.u.) would be expected to balance each other out, if the  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{H}_4\text{Cl}_2$  molecules are really flat and hexagonal in shape. Actually the permanent electric moment of para-dichloro-benzene is really zero, as predicted. In the case of the *meta* compound, where the two moments are no longer directly opposed, but make an angle of about  $120^\circ$  with one another, it is found from the dielectric constant measurements that the electric moment is  $1.48 \times 10^{-18}$ . This result is extremely gratifying, because it is very close to the value that we would predict by arranging two C — Cl moments of  $1.5 \times 10^{-18}$  in this way. And again in the *ortho*-compound, where the angle is only  $60^\circ$  between the two moments, they come much nearer adding up to  $1.5 \times 10^{-18} + 1.5 \times 10^{-18}$  (as they would if the angle between them were  $0^\circ$ , i.e., if they were both pointing in the same direction). The observed value for the electric moment of the *ortho*-compound is  $2.25 \times 10^{-18}$ , which is close to the predicted value.

The electric moment has been determined for a large number of molecules of interesting geometrical structure. We cannot, however, secure the necessary data to calculate the electric moment, with the simple experimental technique which we have described in this experiment. The student should consult Debye's "*Polar Molecules*," The Chemical Catalog Co., 1929; and Smythe's "*Dielectric Constant and Molecular Structure*," The Chemical Catalog Co., 1931.

One may conclude, however, from the observed values for dielectric constants, obtained in this experiment that brombenzene is more polar, or has a larger electric moment, than benzene, and chlorbenzene still larger. Similarly, chlor-acetic acid is much



more polar than acetic acid. In the case of  $\text{CCl}_4$ , the separation of positive and negative charges within the molecule is probably considerable, but is not apparent in the experimental result because of the symmetrical disposition of the four chlorine atoms about the central carbon atom. The electric moments are thus so arranged that they happen to balance out. In the unsymmetrical molecule of  $\text{CHCl}_3$  the moment appears.

REFERENCES:

- Rodebush, Chap. XIII.
- Getman and Daniels, Chap. V.
- Eurken, Jette and LaMer.
- Thomson, *The Electron in Chemistry*.
- Lauer and Brown, *Radio Engineering Principles*.
- Van Der Bijl, *Thermionic Vacuum Tubes*.



## EXPERIMENT 31

### MEASUREMENT OF ELECTRICAL CONDUCTIVITY

One of the most important and interesting properties of an aqueous electrolytic solution is its ability to conduct electricity. The conduction is effected by the ions of the electrolyte and its magnitude is largely dependent upon the number of ions present. The number of ions is in turn dependent upon the concentration of the electrolyte in the solution and also upon the "degree of ionization." Since the "degree of ionization" is an important factor in the electrolytic dissociation theory, the value of conductance measurements at once becomes evident.

Instead of measuring the conductance directly it is determined indirectly from the measurement of the resistance. The specific resistance is the resistance in ohms of a cube of the conductor 1 cm. along an edge. The reciprocal of this is the specific conductance or conductivity and its unit is the reciprocal ohm or mho. Generally the conducting power is expressed as either equivalent or molecular conductance. The equivalent conductance  $\Lambda$  is the conductance in reciprocal ohms of a solution containing one gram equivalent of solute when placed between parallel electrodes 1 cm. apart having an area great enough to enclose such a volume of solution. The molecular conductance  $\mu$  may be defined in the same way except that the volume of solution placed between the electrodes contains one gram molecule instead of one gram equivalent of solute. If  $\kappa$  is the specific conductance,  $V_e$  the volume of solution in cubic centimeters containing one gram equivalent and  $V_m$  the volume containing one gram molecule then

$$\Lambda = \kappa V_e \quad (1)$$

and

$$\mu = \kappa V_m \quad (2)$$

An increase in the dilution results in a decrease in the specific conductance and an increase in the equivalent conductance, because of increasing apparent degree of ionization with dilution.



The latter approaches a limiting value which is termed the equivalent conductance at infinite dilution,  $\Lambda_\infty$ , or at zero concentration,  $\Lambda_0$ . The dilution at which this occurs is different for different electrolytes and represents the concentration at which all of the electrolyte molecules are ionized. Dividing the value for  $\Lambda$  at any one dilution by the value  $\Lambda_\infty$  at infinite dilution should, therefore, give the degree of ionization of the electrolyte at that concentration. Thus

$$\alpha = \frac{\Lambda}{\Lambda_\infty}. \quad (3)$$

The doubtful meaning of  $\alpha$ , however, in the case of strong electrolytes, must be kept in mind. (See Exps. 19, 33, 37.)

The measurement of electrical conductivity is nothing other than a measurement of specific resistance and can best be made

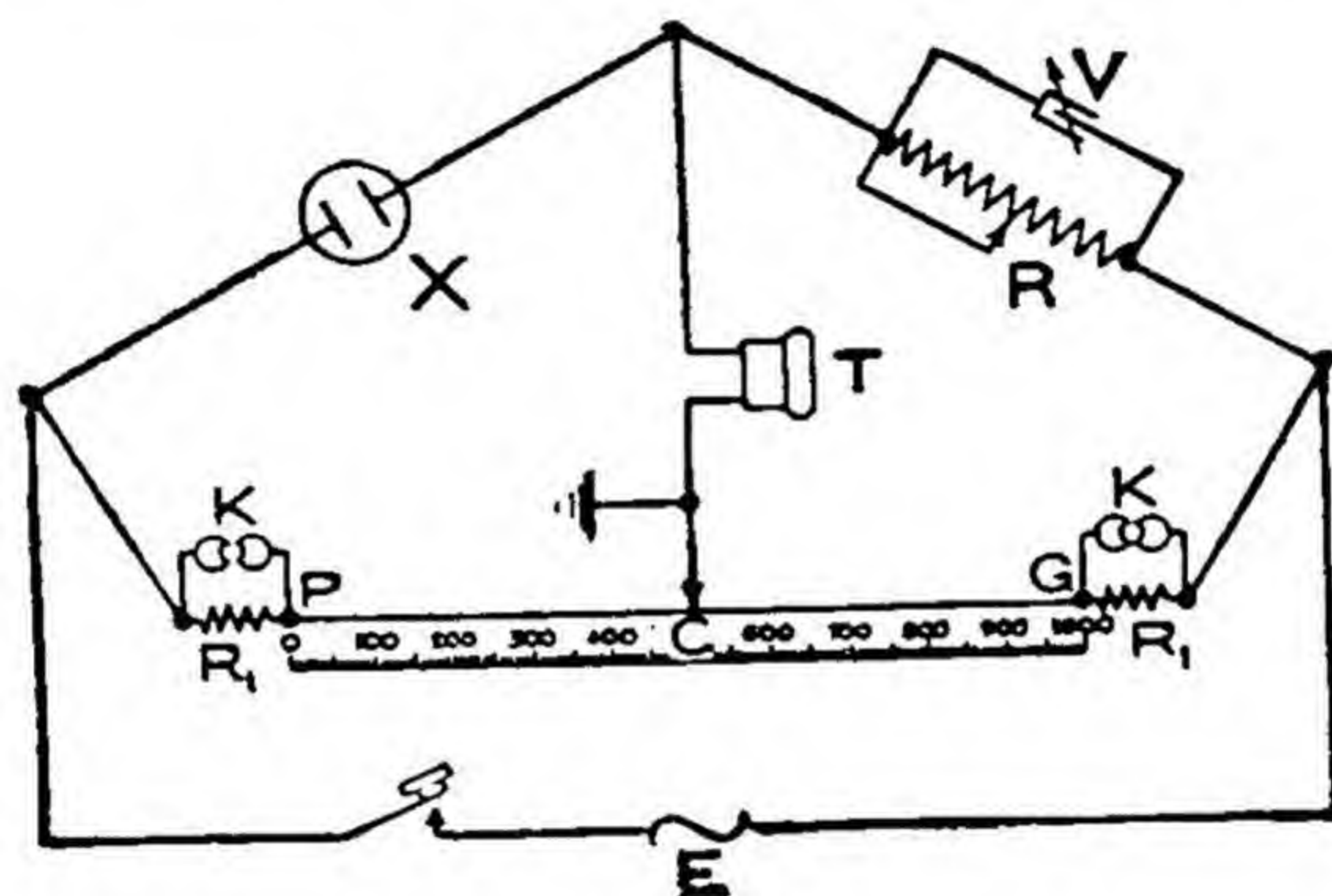


FIG. 56

with a Wheatstone bridge, modified to meet the conditions imposed by the nature of the material whose resistance is desired. Figure 56 shows the arrangement of the apparatus. E is a source of *alternating current* (1000 cycles per second) made necessary to avoid discharging the ions at the electrodes, which would produce changes in the composition of the solution. X is the cell containing the solution whose resistance is desired; R a variable resistance; V a variable air condenser; PG a slide wire of uniform cross sectional area provided at each end with fixed extension coils  $R_1$ ; and T is a telephone receiver connected to the movable contact C. The bridge is balanced when no current flows through the telephone



receiver. The resistance in the cell is then given by the following relation

$$\frac{X}{R} = \frac{PC}{CG} \quad (4)$$

or

$$X = \frac{PC}{CG} R.$$

The position of balance is determined by moving the contact C along the wire until the sound in the telephone receiver produced by E reaches a minimum. For this experiment an induction coil serves as a satisfactory source of current; however, a microphone hummer or, better, a Vreeland oscillator or a thermionic oscillator should be used for accurate work. The condenser V is used to ensure perfect silence when the balance point is reached, by balancing its capacity against that of the cell X. It can be omitted in the present determination. The function of the extension coils is to increase the effective resistance of the slide wire. This wire is generally wound on a revolving drum instead of being stretched out as indicated in the diagram. (For a detailed description of conductivity apparatus see Reilly, *Physico-Chemical Methods*, pp. 577-601.)

The conductance cell is shown in detail in Fig. 57. Before using the cell the electrodes should be freshly coated with platinum black. This is done in order to reduce the polarization effect to a minimum by having the maximum surface area in contact with the solution. The platinizing is accomplished by passing a direct current between the electrodes immersed in a solution containing 3 g. of chloroplatinic acid and 0.02-0.03 g. of lead acetate per 100 cc. of water, and reversing the direction of the current every half minute. When an even velvety black deposit is obtained, the electrodes should be washed in distilled water, placed in dilute sulfuric acid and a current passed between them for 30 minutes, with reversal of current every minute, to remove occluded gases and liquid. The electrodes are then washed in distilled water and finally allowed to stand in conductivity water for a few hours.



FIG. 57



The conductivity of a solution has been defined in terms of the resistance of a centimeter cube. Since it is practically impossible in the present experiment to have electrodes of such dimensions as to enclose exactly between them a centimeter cube, the measured conductance must be multiplied by a factor converting it to the value which would have been obtained if this condition had been met. This factor is called the cell constant or resistance capacity factor, and is dependent upon the area of the electrodes and their distance apart. It is determined by measuring the conductance of a solution having a known specific conductance (conductivity) and solving for  $K$  in the expression

$$Kc = \kappa \quad (5)$$

in which  $\kappa$  is the specific conductance and  $c$  the measured conductance.

#### CONDUCTIVITY WATER

In making up solutions and also in diluting those already made it is essential that quite pure water be used. This requirement is imposed by reason of the great sensitivity of the method employed and the assumption that the conductance measured is due solely to the ions of the solute. The presence of any ions other than those of the solute would modify the conductance and unless corrected for would introduce an error of appreciable magnitude. As carbon dioxide and ammonia are both present in the air and also are quite soluble in water, they constitute the chief impurities present in good distilled water. They can be removed by distilling water to which has been added potassium acid sulfate and barium sulfate, and collecting the distillate out of contact with the laboratory air in hard glass bottles, stoppered with a paraffined cork containing a siphon and a soda lime tube. A very satisfactory conductivity water still is that of Bourdillon (*J. Chem. Soc.*, **103**, 791 (1913)), which is also described by Reilly (*Physico-Chemical Methods*, p. 597). Good conductivity water may be secured by distilling distilled water in quartz vessels. (See also an article by Kendall, *J. Am. Chem. Soc.*, **38**, 2480 (1916).)

#### DETERMINATION OF THE CELL CONSTANT

Prepare 100 cc. of an exactly 0.1000  $M$  potassium chloride solution, using pure recrystallized potassium chloride and good con-



ductivity water. This solution is best made up gravimetrically and should be kept in a hard glass bottle. Having prepared the KCl solution, next platinize the electrodes as directed above, and connect the apparatus as shown in the diagram. Place the conductivity cell containing conductivity water in a thermostat regulated to  $25^{\circ} \pm .05^{\circ}$ . When this temperature has been attained by the solution determine the position of minimum sound on the bridge and about 5 minutes later determine whether it has been changed any. If not, then the temperature of the cell can be assumed to be the same as that of the thermostat. This determination is repeated, using another sample of conductivity water. If the same value is again obtained the cell can be considered as being clean. The cell with its electrodes is next thoroughly rinsed, five or six times at least, with 0.1 *M* KCl solution, then filled and replaced in the thermostat. When the temperature becomes constant determine the position of minimum sound and calculate the cell constant *K*.

If the position of the sliding contact *C* corresponds to a bridge reading of *l* cm. and if the wire is 100 cm. long, then the ratio *PC/CG* becomes  $l/(100 - l)$ . If now *R'* is the resistance of the cell, then

$$\frac{R'}{R} = \frac{l}{100 - l} \quad \text{or} \quad R' = \frac{l}{100 - l} R.$$

The measured conductance is therefore

$$c = \frac{1}{R'} = \frac{100 - l}{Rl}.$$

Hence from Equation 5

$$K = \frac{Rl\kappa}{100 - l}.$$

The cell constant is, therefore, expressed in terms of the resistance *R*, the specific conductance  $\kappa$ , and bridge reading *l*. In calculating *K* use the value 0.01288 mhos for the conductivity of 0.1 *M* KCl at 25°. Having determined the cell constant *K* from three sets of readings obtained with different values of *R*, clean the cell thoroughly and determine the conductivity of the conductivity water used.



If now the resistance in the bridge arm is  $R$  ohms and the point of minimum sound on the bridge is  $l$  cm. then the conductance is equal to  $\frac{100 - l}{Rl}$ . This, multiplied by the cell constant  $K$ , gives the conductivity  $\kappa_0$  of the water used. Thus

$$\kappa_0 = \frac{K}{R} \cdot \frac{100 - l}{l}.$$

### DETERMINATION OF EQUIVALENT CONDUCTANCE OF SILVER NITRATE

Prepare 100 cc. of 0.1000  $M$   $\text{AgNO}_3$  solution, using good conductivity water and recrystallized silver nitrate. The flask containing this solution and a liter flask full of conductivity water, to be used for diluting the solution, should both be kept in the thermostat. Thoroughly clean and dry four 120 cc. hard glass bottles and provide a means of supporting them in the thermostat. With an accurately calibrated 25 cc. delivery pipette, put 25 cc. of the  $M/10$   $\text{AgNO}_3$  in a 100 cc. calibrated flask and dilute to the mark with conductivity water. Both the water and the silver nitrate solution should be at  $25^\circ$ . Mix thoroughly and pour into one of the 120 cc. bottles previously placed in the thermostat. Clean and dry the pipette and flask. With the pipette put 25 cc. of the  $M/40$   $\text{AgNO}_3$  solution in the flask and dilute to 100 cc. as before. When thoroughly mixed pour this  $M/160$   $\text{AgNO}_3$  solution in the second hard glass bottle. In the same way make  $M/640$  and  $M/2560$  solutions.

Next clean the conductivity cell and electrodes with conductivity water. Dry the electrodes and rinse with the  $M/10$   $\text{AgNO}_3$  solution. Fill the cell, place it in the thermostat and determine the conductivity as before. Make three different sets of readings with different values of  $R$ . It is advisable to adjust the resistance  $R$  so as to bring the point of balance in the middle portion of the bridge wire. From the values for the specific conductance calculate the equivalent conductance for each dilution, using Equation 1. This, in terms of  $R$ ,  $K$ ,  $l$  and the dilution  $V$ , which is the volume of solution containing one mol of solute, takes the form

$$\Lambda = \frac{K}{R} \frac{100 - l}{l} V.$$



Tabulate your data and plot the equivalent conductances against the concentration. Extrapolate this curve to zero concentration (infinite dilution). Using the value for  $\Lambda$  at infinite dilution calculate the "degree of ionization" for  $\text{AgNO}_3$  at each of the other dilutions.

#### INFLUENCE OF TEMPERATURE ON CONDUCTIVITY

Determine the conductivity of the  $M/40$   $\text{AgNO}_3$  solution exactly as at  $25^\circ$ , but at each of the following temperatures:  $30^\circ$ ,  $35^\circ$  and  $40^\circ$ . Use a large beaker of water as a thermostat. Plot the values obtained against the temperature and draw the curve showing this relationship. Compare the change in conductivity with temperature with that of viscosity of water with temperature (Exp. 10).

Among the many interesting and valuable applications of conductivity measurements are to be found the determination of an end point in a titration and the determination of the solubility of a slightly soluble salt. These applications are illustrated in the following experiments on "The conductimetric titration of a solution of  $\text{HCl}$  with  $\text{NaOH}$ " and "The determination of the solubilities of  $\text{BaSO}_4$  and  $\text{Ag}_2\text{CrO}_4$ ."

#### THE CONDUCTIMETRIC TITRATION OF AN $\text{HCl}$ SOLUTION WITH $\text{NaOH}$

This method depends upon the fact that among other things the conductance of a solution is a function not only of the concentration of the ions but also of the ionic velocities. Any marked change in either or both of these factors results in a change in the conductance. Thus in the case of the neutralization of a strong acid by a strong base, if one adds a solution of the base to the acid, the salt of the acid and water are formed with the result that the faster moving  $\text{H}^+$  ions are replaced by the slower moving cations of the base. Since the difference in the degree of ionization of the salt and the acid is negligible, successive additions of the base to the acid gradually lower the conductance still further until a minimum value is reached when all the  $\text{H}^+$  ions of the acid have been removed, that is until the neutralization is complete. Further additions of the base beyond this point will then markedly increase



the conductance because of the considerable increase in the concentration of the free and fast moving  $\text{OH}^-$ .

A known volume of  $\text{HCl}$  solution sufficient to cover the electrodes is put in the conductivity cell and the position of balance on the bridge wire is determined following the same procedure and observing the same precautions as in the earlier experiments. The position of balance is again determined after each addition of successive small quantities of standard  $\text{NaOH}$  solution. A good calibrated burette should be used and the solution thoroughly mixed before the bridge reading is determined. The resistance  $R$  should be so chosen that the initial point of balance is obtained about the middle of the bridge wire and it should not be changed during the course of the neutralization. The bridge readings corresponding to the number of cc. of standard  $\text{NaOH}$  added are plotted as ordinates against the number of cc. of  $\text{NaOH}$  as abscissas and the curves connecting the points drawn. The intersection of the two curves indicates the number of cc. of standard base required for the neutralization. The determination can be checked by having a few drops of phenolphthalein present in the  $\text{HCl}$  solution.

#### THE SOLUBILITIES OF $\text{BaSO}_4$ AND $\text{Ag}_2\text{CrO}_4$ IN WATER AT $25^\circ$

In general it may be assumed without serious error that a saturated solution of a slightly soluble salt is completely ionized. On the basis of this assumption then  $\Lambda_\infty$  may be regarded in such a case as equal to  $\Lambda$  and Equation 1 above may be written as

$$\Lambda_\infty = \Lambda = \kappa V_e \quad (6)$$

If now the solubility of the salt in gram equivalents per liter is represented by  $S$  then  $\frac{1000}{S}$  cc. is the volume,  $V_e$ , containing one gram equivalent and Equation 6 becomes

$$\Lambda_\infty = \frac{\kappa \cdot 1000}{S} \quad (7)$$

from which

$$S = \frac{\kappa \cdot 1000}{\Lambda_\infty} \quad (8)$$

It is evident therefore that the solubility in gram equivalents



per liter can be determined from a knowledge of the specific conductance,  $\kappa$ , of a saturated solution of the salt and  $\Lambda_{\infty}$ , the sum of the ionic conductances of the cation and anion of the salt.

The salts  $\text{BaSO}_4$  and  $\text{Ag}_2\text{CrO}_4$  are first finely ground and thoroughly washed with conductivity water to remove any soluble impurities which may be present. About 10 g. of the salt are then placed in a 250 cc. Erlenmeyer flask, thoroughly shaken with about 200 cc. of high grade conductivity water at 10–15 minute intervals for about 2 hours. During these intervals the flask and contents are kept in a thermostat maintained at a temperature of  $25^\circ$ . A portion of the solution is then placed in a conductivity cell having large electrodes rather close together and the specific conductance is determined. The determination is repeated at 15–30 minute intervals with fresh portions of the solution until a constant value is obtained. The specific conductance so determined is then corrected by subtracting the conductivity of the water used from this value. The solubility is then calculated as indicated above in Equation 8. The ionic conductances may be found in handbook tables.

Compare the value obtained in this experiment for the solubility of  $\text{Ag}_2\text{CrO}_4$  with that obtained in Experiment 33. Which do you regard as the more accurate and why?

REFERENCES:

- Taylor, Chap. XI.
- Rodebush, Chap. X.
- Getman and Daniels, Chap. XV.
- Millard, Chap. VI.
- Findlay, Chap. IX.



## EXPERIMENT 32

### TRANSPORT NUMBERS; COULOMETERS AND CONDUCTANCE OF GLASS

In the following experiment one of the usual procedures for the determination of transport numbers is adopted with the exception that a simple means is here provided for rectifying an alternating current, so that an ordinary 110 volt a.c. electric light current may be employed. The rectifier consists of a bath of molten sodium nitrate (and about 5% sodium chloride to lower the melting point) in which is partially immersed an electric light bulb, the filament of which is heated with an alternating current in the usual manner. The hot filament gives off electrons, and when a negative charge (from the alternating current) is being imposed upon the filament, some of these electrons are repelled and at the same time some of the small, mobile, positively charged sodium ions are pulled into the bulb from the hot glass surface. The sodium ions are soon neutralized by captured electrons and the sodium vapor thus formed deposits as metallic sodium on the cooler portions of the electric light bulb, where it is not immersed in the hot bath. The loss of electrons by the filament and loss of sodium ions by the glass are both equivalent to a flow of negative electricity from the filament to the glass. Sodium ions from the sodium nitrate bath replace those lost by the glass, and at the same time nitrate ions are discharged at a positively charged metallic electrode (the metal vessel containing the melt). On the other hand, when the filament becomes positively charged, there is no flow of current, since there are no negatively charged ions present in the glass which are mobile enough to move, and since the filament does not, of course, give off positively charged ions. For these reasons the alternating current is rectified, an intermittent unidirectional current being obtained. This rectifier (see Burt, *J. Optical Soc. Am.*, **11**, 87 (1925)) illustrates a number of interesting points; for example, it serves as a fairly good coulometer, or, if the current which passes is known, the atomic weight of sodium



may be calculated from the weight of metallic sodium which collects inside the glass bulb. The experiment suggests that glass is a *liquid*, although a very viscous one, since it permits the passage of ions by electrolysis. It also gives a very fine method for the preparation of pure sodium in small amounts.

As some of the newer type bulbs are made from rather hard glass through which the ions diffuse with difficulty, care should be taken to select either an old carbon filament or a 40–60 watt tungsten filament bulb of plain unfrosted glass. Gas-filled bulbs should also be avoided. The clear glass 50-watt "Mill Type" bulb (either General Electric or Westinghouse) works very satisfactorily.

#### EXPERIMENTAL

Figure 58 shows the arrangement of the apparatus. Both legs A and C, and the middle section M, of the transport tube are filled

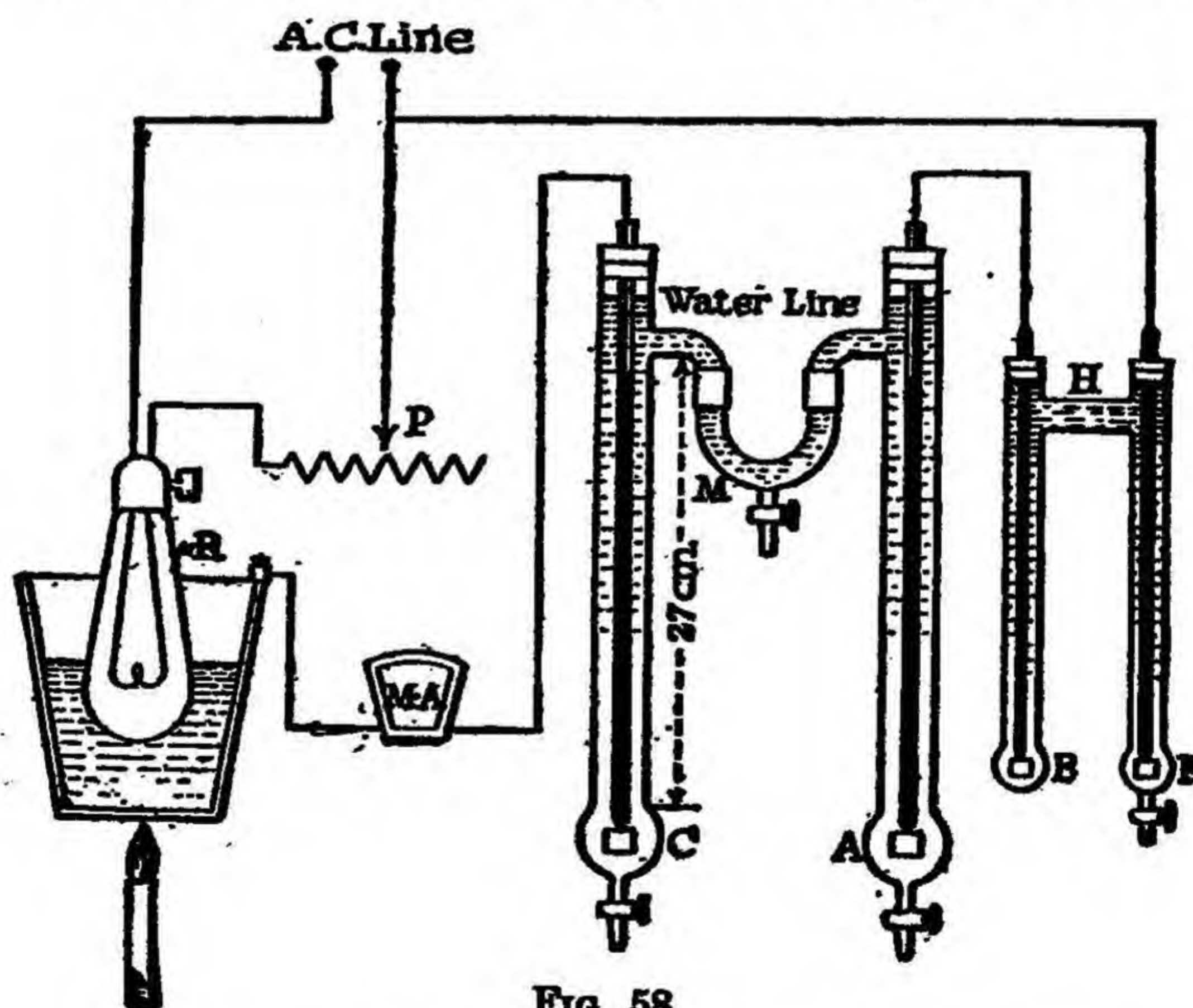


FIG. 58

with about 0.1 *N* solution of silver nitrate. The middle section M, provided with a stop-cock, may be attached to the legs with large sized rubber tubing or with ground glass joints. It is important that the legs be rather long. The dimensions indicated in the figure are satisfactory. The two electrodes at A and C are



of platinum foil supported in glass tubes and provided with mercury leads. The anode A must be previously plated with silver (or it may be made of *pure* silver — copper-free). In the silver plating use a bath of silver cyanide, made by dissolving 15 g. of silver nitrate and 20 g. of potassium cyanide in a liter of water. In plating, a silver coin may be used as anode, provided the current density is not too high (not over 7 milli-amperes per cm.<sup>2</sup>).

The iodine coulometer, also equipped with platinum electrodes, is filled in both legs with 10 per cent potassium iodide solution up to within a few centimeters of the cross tube H. Then 10 cc. of 50 per cent potassium iodide solution is introduced into bulb F through a long capillary funnel (made by drawing out a small test tube or vaccine tube) which extends down to the bottom of the bulb. In this way the stronger solution is introduced *without* mixing with the 10 per cent potassium iodide solution above it. In the same way introduce into bulb E 2 or 3 cc. of the 50 per cent potassium iodide solution and then underneath this 10 cc. of a 50 per cent potassium iodide solution saturated with iodine. Leave the capillary funnel in E (the cathode chamber) or withdraw it *very slowly and carefully*, to avoid mixing of the layers. When both bulbs E and F have been loaded, the solution of 10 per cent potassium iodide should then fill the connecting tube H.

The strength of the rectified current which is allowed to flow through the transport number tube and the iodine coulometer which are connected in series as shown in the diagram, is controlled in two ways, (1) by changing the amount of the glass surface of the electric light bulb R, immersed in the molten salt, and (2) by moving the rheostat contact P to regulate the filament heating current. The temperature of the filament should be kept as low as possible in order to lengthen the life of the bulb, for in the presence of sodium vapor the tungsten filament sometimes burns out during the course of the determination.

A current of 8–10 milli-amperes, as measured on the milli-ampere meter M.A., is sent through the system for about 2 or 3 hours. It is important that the current density should not be too high, about 0.5–1 milli-ampere per cm.<sup>2</sup> of surface of the cathode C in the transport number tube, and not more than 5 milli-amperes per cm.<sup>2</sup> of anode F surface in the iodine coulometer.



The quantity of electricity which has passed is estimated roughly from the meter reading and the time (remember that the current, which is intermittent, is on only half the time), and is calculated more exactly from the volume of standard thiosulfate solution (0.02 *N*) required to titrate the iodine liberated at the anode *F* (this should be run out through the stop-cock into a beaker for titration). The concentrations of silver nitrate in legs *A* and *C* and the middle portion *M* are determined by removing most of the solution in each section through the stop-cocks, taking care not to wash down loose crystals of silver, weighing the solutions in beakers, and then adding an excess of sodium chloride solution and titrating back with standard silver nitrate solution, using sodium chromate as an indicator. If the concentration in the middle portion has changed, the time was too long and the experiment must be repeated in a shorter time.

Care must be taken that the apparatus is not subjected to vibrations, such as those from a motor. If it is observed that the menisci in the transport tube dance up and down, these vibrations must first be removed or else absorbed by placing some sort of cushion (even an ordinary book is often very efficient) underneath the stand supporting the transport tube.

Calculate the atomic weight of sodium from the gain in weight of the electric light bulb. Calculate the transport numbers of  $\text{Ag}^+$  and  $\text{NO}_3^-$  from the change in concentration in the anolyte and catholyte. Calculate the concentrations on a weight basis. It is permissible to take the average of the anolyte and catholyte concentration changes for the transport number calculation. From the transport numbers of  $\text{Ag}^+$  and  $\text{NO}_3^-$ , and from the result for the equivalent conductivity at infinite dilution of silver nitrate obtained in Exp. 31, calculate the ionic conductivities of  $\text{Ag}^+$  and  $\text{NO}_3^-$ . Calculate the velocity in cm. per sec. with which silver ions move under a potential gradient of one volt per cm. (See Taylor, pp. 397–402.) Estimate the area of the glass bulb in contact with the molten sodium nitrate and, taking the average thickness of the glass as 0.7 mm., or whatever it seems to be, and the potential drop across the glass as 20 volts, calculate the resistivity and conductivity of the glass under the conditions of this experiment. When a current of 10 milli-amperes is indicated by the meter, what is the total number of electrons which are captured by sodium ions in



one second? What would be the weight in grams of this number of electrons?

### OTHER COULOMETERS

If the deposition of Ag on the cathode C, Fig. 58, could be followed quantitatively, by weighing before and after the run, the total quantity of electricity which flows could be calculated from the silver equivalent, namely 0.0011180 g. Ag per coulomb. But the form of the electrode, i.e., the attached glass tubing containing mercury, and the copper wire dipping into the mercury, would make such a weighing far from reliable. However, a silver weight coulometer, and a copper weight coulometer, and a gas coulometer may altogether, or separately, be inserted into the circuit in series with the iodine coulometer, or these coulometers may be run in series in a separate experiment, if the student cares to do so, to determine the several Faraday equivalents.

**Silver Coulometer.** The silver weight coulometer, of all coulometers, is generally regarded as being capable of producing the most accurate results. It is used as a standard in the determination of the value of the Faraday unit and in defining the coulomb and ampere. One convenient form makes use of a small platinum crucible as cathode, containing a 10–20% solution of  $\text{AgNO}_3$ . An anode of electrolytically deposited Ag surrounded by a small porous cup or paper extraction thimble is immersed and suspended in the  $\text{AgNO}_3$  solution. The purpose of the porous cup is to catch any material falling off the anode during electrolysis.

The platinum crucible is weighed before and after the passage of the current. The current density should not be greater than 0.02 amp./cm.<sup>2</sup> of cathode surface. Since the deposit of Ag consists of rather large loosely adherent crystals, great care must be taken in washing out the  $\text{AgNO}_3$  solution at the end of the run, preparatory to drying and weighing. The washing can best be accomplished by removing the successive additions of wash water from the crucible with a pipette, until the washings are free from  $\text{Ag}^+$ , as shown by failure to get even a faint precipitate with NaCl solution.

**Copper Coulometer.** The copper weight coulometer affords less accurate measurements than the silver weight coulometer. Its advantage lies in its greater convenience and ease of operation. A



400–500 cc. beaker fitted with a non-conducting lid provided with suitable openings for a stirrer and the electrodes serves as a satisfactory vessel. The electrolyte has the following composition: 150 g.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; 50 g. conc.  $\text{H}_2\text{SO}_4$ ; and 50 cc. ethyl alcohol in a liter of distilled water. A cathode of electrolytic sheet copper is suspended vertically in the center of the beaker and two anodes of like material are suspended on both sides of the cathode. The electrolyte is stirred gently during the electrolysis either with a mechanical stirrer or by slowly bubbling in  $\text{CO}_2$ . After the electrolysis, the cathode is washed thoroughly with distilled water, then rinsed in alcohol and dried and weighed. The cathode current density may vary from 0.02–0.002 amp./ $\text{cm}^2$ . The electrochemical equivalent of cupric copper is 0.0003294 g.

**Gas Coulometer.** The gas coulometer is less accurate than either the silver or copper weight coulometers, but possesses the advantage of not requiring any weighings. It may be made from a 100 cc. burette which has an enlarged opening at the top capable of admitting a No. 8 3-hole rubber stopper. This can be done by sealing glass tubing of correct size to the top of the burette, which is used in an inverted position, that is with the stop-cock up. Nickel electrodes are inserted through two of the holes in the rubber stopper and a glass tube connected by means of rubber tubing to a leveling bottle is inserted through the third hole. The electrolyte is a 10%  $\text{NaOH}$  solution. The inverted burette and leveling bottle are supported on an iron ring stand. The stop-cock is opened and the burette is filled to the top graduation by raising the leveling bulb. The stop-cock is then closed and the electrolysis begun, at the end of which the volume of mixed gas is determined and corrected to N.T.P.

One Faraday of electricity will liberate 16.78 liters of dry mixed hydrogen and oxygen at  $0^\circ$  and 760 mm. pressure. Therefore 1 cc. corresponds to 5.75 coulombs. Before putting the gas coulometer in service after the introduction of fresh electrolyte it is necessary to electrolyze the solution for a while in order to saturate it with the gases and also because a fresh solution of  $\text{NaOH}$  foams considerably.



REFERENCES:

- Taylor, Chap. XI.
- Rodebush, Chap. X.
- Getman and Daniels, Chap. XV.
- Millard, Chap. VI.
- Findlay, Chap. IX.
- Eucken, Jette and LaMer.



## EXPERIMENT 33

### CONCENTRATION CELL AND SOLUBILITY PRODUCT

The following experiment illustrates a number of important principles. It gives a method for determining the values of the solubility and the solubility product of a slightly soluble substance such as silver chromate. Because of the simplification necessary for our present purpose, the values so obtained, however, cannot be considered accurate, but only of the correct order of magnitude. (For an excellent discussion of solubility product, see Stieglitz, *Qualitative Chemical Analysis, Theoretical Part*, Chapter VIII.)

#### EXPERIMENTAL

(a) Place two beakers (100 cc.), each one containing 50.0 cc.  $10^{-3} M$   $\text{Na}_2\text{CrO}_4$  solution, on a piece of black paper or other dark background. Keeping one beaker and solution as a control, determine accurately the volume of  $0.01 M$   $\text{AgNO}_3$  solution which must be added to the other until a barely perceptible reddish turbidity is produced. Any small precipitate formed locally disappears on stirring. Further addition of  $\text{AgNO}_3$  solution beyond the end-point forms a permanent precipitate. The appearance of the turbidity, which is taken as the end-point, can be readily observed only by comparing with the control. A 1 cc. burette, or a 1 cc. pipette with a scale indicating 0.01 cc. and provided with a stop-cock or thumb-screw rubber-tube outlet, should be employed to deliver the  $\text{AgNO}_3$  solution. Repeat several times as a check. From your measurements calculate the solubility at room temperature of  $\text{Ag}_2\text{CrO}_4$ , expressed as grams per 100 cc. and as mols per liter. Calculate the solubility product, remembering that the silver ion concentration term must be *squared*, and compare the result with the accepted value.

(b) Arrange a concentration cell as shown in Fig. 59. The two silver wire electrodes A and B must first be lightly silver-plated, using a silver anode, the silver cyanide solution already



mentioned (in Exp. 32), and a cathode current density a little less than 1 milli-ampere per  $\text{cm}^2$ , for a few minutes. The silver electrodes, attached to copper wires, are sealed into the ends of short glass tubes with De Khotinsky cement, or with sealing wax. The glass tubes are then supported in cork or rubber stoppers in the two legs of the cell. The beaker M contains a saturated solution of  $\text{NH}_4\text{NO}_3$ , into which dip the two goose-neck tubes from the two legs. This arrangement largely reduces the contact potential which would otherwise exist at the junction of two solutions of different ion concentrations contained in the cell legs.

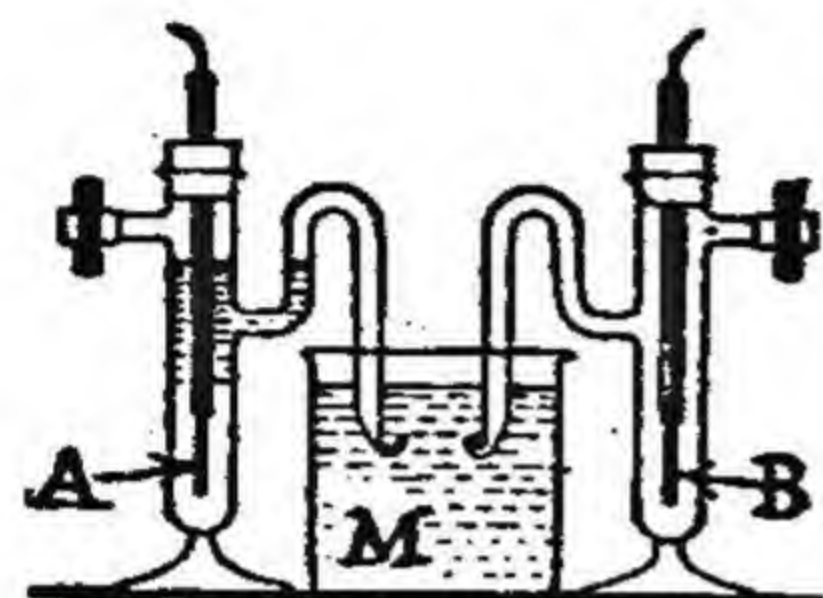


FIG. 59

First, introduce 0.1  $M$   $\text{AgNO}_3$  solution into each leg, so that the two side-tubes are filled, and using the potentiometer system to be described (in Exp. 34), make sure that the E.M.F. of the cell is practically zero (it should not be larger than 0.001 volt). Solid electrodes in general are not very satisfactory because of the difficulty of reproducibility, that is, in the present case, the nature of the metallic silver surface of electrode A may be slightly different from that of B, and hence a difference of potential is set up.

Now, (1) replace the 0.1  $M$   $\text{AgNO}_3$  solution at B with 0.05  $M$   $\text{AgNO}_3$  solution, and (2) finally with 0.01  $M$  solution, in each case measuring the E.M.F. of the cell after a constant reading has been attained. Assuming that the activity coefficients of the 0.1, 0.05 and 0.01  $M$   $\text{AgNO}_3$  solutions are respectively, 0.723, 0.783, and 0.902 calculate the E.M.F.  $E$  of the concentration cells (1) and (2) above by means of the Nernst equation

$$E = \frac{RT}{nF} \ln \frac{\gamma_1 m_1}{\gamma_2 m_2} = \frac{RT}{nF} \ln \frac{a_1}{a_2}$$

where  $\gamma$ ,  $m$  and  $a$  represent respectively activity coefficient, molality, and activity, and compare with your measured voltages.

(c) Replace the  $\text{AgNO}_3$  solution at B with a stock 0.1  $M$   $\text{Na}_2\text{CrO}_4$  solution saturated with  $\text{Ag}_2\text{CrO}_4$ , and from the measured E.M.F. of the cell, calculate the concentration of the silver ions, and then the solubility of  $\text{Ag}_2\text{CrO}_4$  (grams per 100 cc. and mols per liter) and finally the solubility product. Compare with the result obtained in (a) above.



The student should read Langmuir's inspiring Chandler Lecture, *J. Ind. Eng. Chem.*, 22, 390 (1930). In it he gives a Boltzmann factor derivation of the Nernst equation, above.

Consider one of the electrodes dipping into an  $\text{Ag}^+$  ion solution. The silver electrode is positively charged (small solution pressure) with respect to the solution. Say the potential difference is  $E'$ . Then, the work  $w$  required to move one silver ion,  $\text{Ag}^+$ , from the solution into the silver electrode surface is,  $w = E' \cdot q$ , where  $q$  is the charge on a silver ion (also on an electron). From the Boltzmann law (see Exercise III) it follows that

$$\frac{N_s}{N_l'} = e^{-\frac{w}{kT}} = e^{-\frac{E' \cdot q}{kT}}$$

where  $N_s$  and  $N_l'$  are the numbers of  $\text{Ag}^+$  per cc. in the two different energy states, namely in the solid surface and in the liquid. Also, by inverting, we have

$$\frac{N_l'}{N_s} = e^{\frac{E' \cdot q}{kT}}.$$

Taking logarithms of both sides,

$$\ln \frac{N_l'}{N_s} = \frac{E' \cdot q}{kT}.$$

Multiplying both  $q$  and  $k$  by the Avogadro number,  $6.06 \times 10^{23}$ , we get

$$\ln \frac{N_l'}{N_s} = \frac{E' \cdot F}{RT}$$

where  $F$  is the Faraday, the total charge on a gram-ion ( $6.06 \times 10^{23}$  particles) of silver ions. If the valence of the ion happened to be  $n$ , 2, 3, 4, etc., the total work done in transporting a whole gram-ion up the potential gradient would of course be  $E \cdot nF$ , and the equation becomes

$$\ln \frac{N_l'}{N_s} = \frac{E' \cdot nF}{RT}.$$

This is the Nernst equation for a single electrode potential. Suppose now that this equation, as stated, is for the silver electrode dipping into the more concentrated  $\text{Ag}^+$  solution in the concen-



tration cell. Let us also state it for the weaker solution, the other half cell:

$$\ln \frac{N_1''}{N_s} = \frac{E'' \cdot nF}{RT}.$$

Subtracting the latter from the former equation, we have

$$\ln \frac{N_1'}{N_1''} = \frac{nF}{RT} (E' - E'')$$

since  $(-\ln N_s + \ln N_s)$  cancels out. The term  $N_s$  is some function of the hypothetical solution pressure of the solid silver and may be assumed to be the same for both electrodes. Since the E.M.F.  $E$  of the concentration cell is  $(E' - E'')$  and since we may use activities,  $a_1$  and  $a_2$ , instead of the effective ion concentrations  $N_1'$  and  $N_1''$ , we finally arrive, if we agree to neglect the boundary potential at the junction of the two ion solutions (only a small correction), at the equation

$$E = \frac{RT}{nF} \ln \frac{a_1}{a_2}.$$

#### REFERENCES:

- Taylor, Chap. XIII.
- Rodebush, Chaps. IX and XI.
- Getman and Daniels, Chaps. XVI and XVII.
- Millard, Chaps. IX and XVII.
- Findlay, Chaps. XV and XVI.



## EXPERIMENT 34

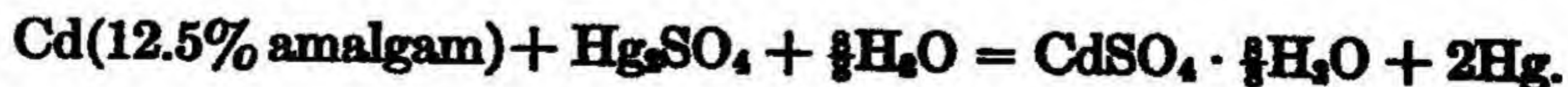
### PREPARATION OF A STANDARD CELL

The junction formed by the contact of a metal and a solution of its ions is the seat of a potential difference, arising according to the Nernst theory from the equilibrium established between two opposing forces, one the tendency of the metal to send ions into the solution and the other the tendency of the ions already present in the solution to deposit out on the metal. The former force is termed the "electrolytic solution pressure of the metal," and the latter the "osmotic pressure of the metal ions in the solution." A galvanic cell consists of a combination of two such junctions, the arrangement being such that when the metals are joined by a wire electricity flows (externally) from one metal to the other and (internally) in the cell from metal to solution, solution to solution, if more than one solution is present, and from solution to metal, thus establishing a complete electrical circuit.

To determine experimentally the value of the electromotive force of any given cell it is first necessary to have a standard source of E.M.F. such that a definitely known, reproducible and constant value shall always be given. For this purpose the Weston standard cell is generally used. One electrode is composed of a 10–15 per cent cadmium amalgam in contact with a saturated solution of cadmium sulfate containing  $\text{CdSO}_4 \cdot \frac{3}{8}\text{H}_2\text{O}$  crystals. The other electrode consists of mercury in contact with a paste of solid mercurous sulfate in a saturated cadmium sulfate solution. The cell is in stable equilibrium when no electricity flows through it and its E.M.F. at  $20^\circ$  is 1.0183 volts. At  $t^\circ$  C. it is

$$E_t = 1.0183 - 0.000038 (t^\circ - 20).$$

The cell reaction when electrical energy is produced is given by the equation



Since the potential ( $E_{\text{re}} = 1.0181$ ) is that of the equilibrium state, i.e., when no electricity flows through the cell, it is obvious



that in order to maintain this constant potential the equilibrium must not be disturbed either by permitting the cell to produce electricity or by passing electricity through it in the reverse direction. The reaction would proceed from left to right in the former case and from right to left in the latter. To prevent these reactions with their resultant equilibrium displacements it is imperative that a null method be used for measuring the potential. The Poggendorf compensation method as incorporated in the various potentiometers is most frequently used for such potential measurements.

### PREPARATION OF CELL

Materials required: Four H-tubes (Fig. 60), twice distilled mercury, 12.5 per cent cadmium amalgam, cadmium sulfate crystals, saturated cadmium sulfate solution, and mercurous sulfate. (For the preparation of these substances the student may refer to Reilly, *Physico-Chemical Methods*, pp. 607-8; and also Hulett, *Physical Review*, 32, 257-80 (1911).) Detailed directions are also given here.

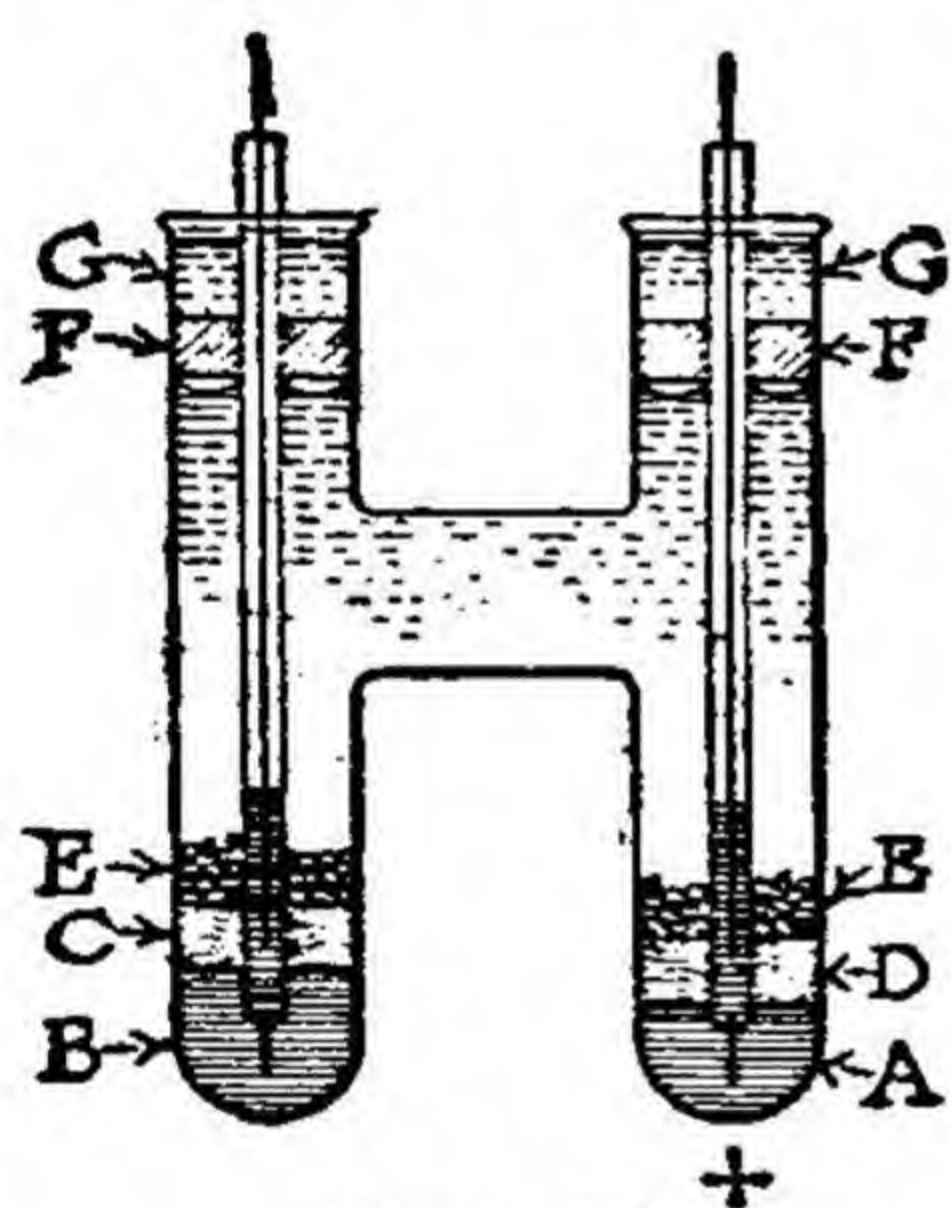


FIG. 60

After securing the above materials and thoroughly cleaning and drying the H-tubes, the cells are then made up as follows: Place a funnel in the right-hand limb of the tube and pour in about 1 cc. of mercury, A. Place the bottle containing the cadmium amalgam in

a dish of water and heat until the amalgam becomes liquid. With a warm pipette remove about 1 cc. of liquid amalgam and put it in the bottom of the other limb, B. Next cover the amalgam with a layer of finely powdered cadmium sulfate crystals about 3 mm. deep, C. A layer D of similar thickness consisting of a paste of mercury, mercurous sulfate, and cadmium sulfate is then placed over the mercury. A few large crystals of cadmium sulfate E are placed in each limb, and a saturated solution of cadmium sulfate in water added until the liquid is up over the cross tube. Leads are inserted through corks, and are made of small glass tubing, with a platinum wire sealed in one end, filled with mercury in which a copper wire is inserted. The tubing is



best filled with mercury by letting it flow through a capillary which reaches to the bottom. The corks FF are cut so as to barely fit the tube, and over them are placed layers of paraffin GG which effectually seal the contents of the tube.

After the cells are made they are placed in a thermostat at  $25.0^{\circ}\text{C.}$ , and their voltages read at intervals with a sensitive potentiometer. After a week or so the cell readings should not vary more than one in the fifth place from day to day.

The "unsaturated" type of the Weston cell may also be prepared. It is made in exactly the same manner as above, except that the  $\text{CdSO}_4$  solution is saturated at  $4^{\circ}$ , and hence is unsaturated at room temperatures. Of course no crystals of  $\text{CdSO}_4 \cdot \frac{3}{8}\text{H}_2\text{O}$  are introduced into the cell. The great advantage of the unsaturated cell is its extremely small temperature coefficient.

#### USE OF THE POTENTIOMETER

The potentiometer, as the name implies, is an instrument for the measurement of potentials. The Poggendorf compensation method is the basis of many potentiometer methods and consists of the necessary electrical circuits such that the potential to be measured is just balanced against an equal and opposite potential of known value. This is illustrated by the diagram of Fig. 61, in which a lead storage cell P is connected to the ends of a wire AB. This wire is of uniform cross sectional area and there will, therefore, be a uniform fall of potential along its entire length. Thus the fall over the portion indicated by AC will be proportional to this length and will equal  $AC/AB$  of the fall across the terminals AB. A standard cell  $E_s$  is connected to the end A of the wire and to the movable contact C through a key  $K_s$  and a galvanometer G. Similarly, the cell  $E_x$  whose electromotive force (E.M.F.) is desired is connected by means of a key  $K_x$ . The arrangement, however, is such that only one of these cells can be in the circuit at the same time. It is further necessary that these cells have a lower E.M.F. than the battery P and also be connected so that they will be working in opposition to it. With key  $K_s$  closed a

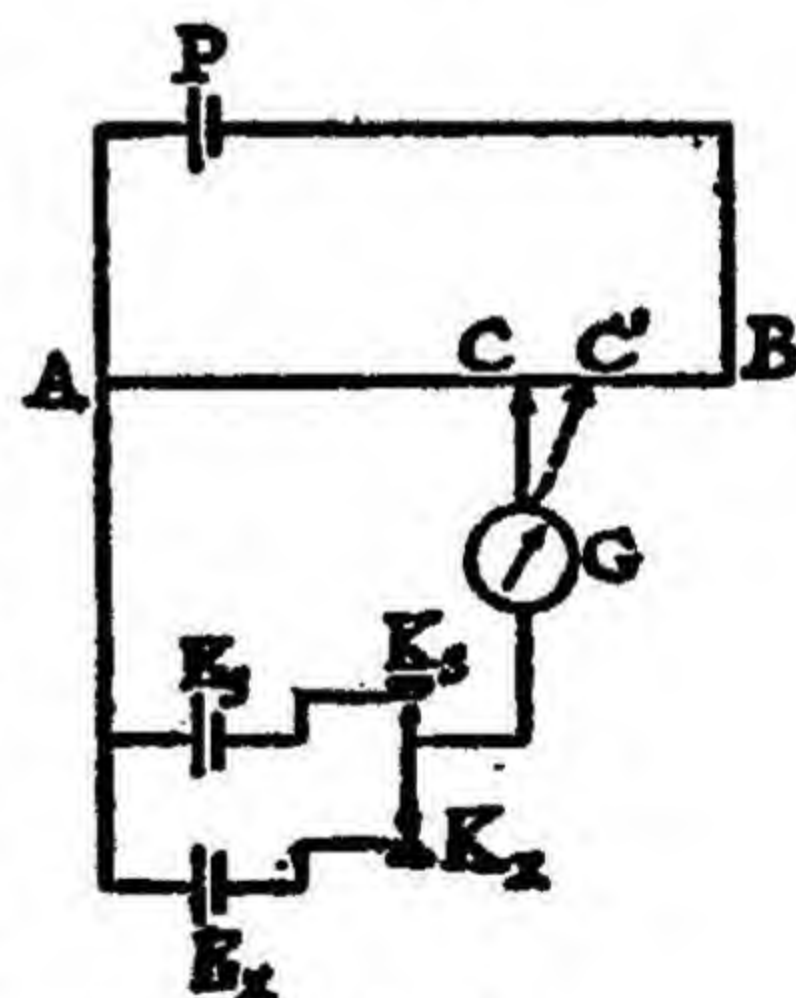


FIG. 61



current will flow through the circuit  $AE_sK_sGC$  at any position of the movable contact except that at which the fall of potential along the wire  $AC$  is equal to the E.M.F. of the cell  $E_s$ . This position is determined by the absence of a galvanometer deflection. Under these conditions the following relation holds:

$$\text{Fall of potential } AB : \text{E.M.F. of } E_s = AB : AC$$

Similarly when a new point of balance  $C$  is determined with the cell  $E_x$  in the circuit the relation is

$$\text{Fall of potential } AB : \text{E.M.F. of } E_x = AB : AC'$$

Combining these proportions we get

$$\text{E.M.F. of } E_s : \text{E.M.F. of } E_x = AC : AC'$$

Therefore

$$E_x = \frac{AC'}{AC} E_s.$$

The essential difference between this simple illustration of the Poggendorf compensation method and a potentiometer is that the latter instrument is made direct reading and much more sensitive by substituting a series of coils of definite resistance for the wire  $AB$  and providing a means of controlling the fall of potential in the storage battery circuit.

Before using the potentiometer read the directions furnished with the instrument. Most instruments contain a high resistance in the galvanometer circuit, which is used to get an approximate balance and is finally cut out entirely when the final balance is obtained. This simply serves as a protection to the galvanometer and to *the standard cell* and should be added if it is not already a part of the potentiometer.

**Purification of Mercury.** The mercury to be purified is first cleaned chemically by shaking it violently for several minutes in contact with dilute  $\text{HNO}_3$  or a solution of  $\text{HgNO}_3$  in a large separatory funnel. Then it is run through Victor Meyer's purification apparatus, Fig. 62. The mercury enters through a special sieve (made by binding a piece of cloth over the flat end of a small funnel) which causes it to split up into a spray of fine droplets. The long vertical tube is filled up with a dilute solution of  $\text{HgNO}_3$ , after enough mercury has been placed in the shorter up-turned



tube at the bottom to balance, hydrostatically, the head of  $\text{HgNO}_3$  solution. The mercury which falls to the bottom is run off through the siphon as shown in the figure. Several passages through the  $\text{HgNO}_3$  solution are desirable. This chemical purification depends on the ability of most metals to displace mercury from solution. Reactions of this sort are however somewhat reversible, even in the case of such strongly electro-positive metals as zinc and cadmium (often present as impurities in mercury).

This chemically cleaned mercury is then introduced into a still, of the type shown in Fig. 63, and heated either with a small electric "cup" furnace, or with a Bunsen flame. The full force of a good water suction pump is applied and a fairly rapid stream of bubbles of air is allowed to come up through the mercury, by adjusting the stop-cock C. The bubbling of air through the capillary (at about 20 mm. pressure) serves two purposes: (1) to stir up the mercury and prevent "bumping"; (2) to oxidize all oxidizable metal impurities. (Some mercury also is oxidized, of

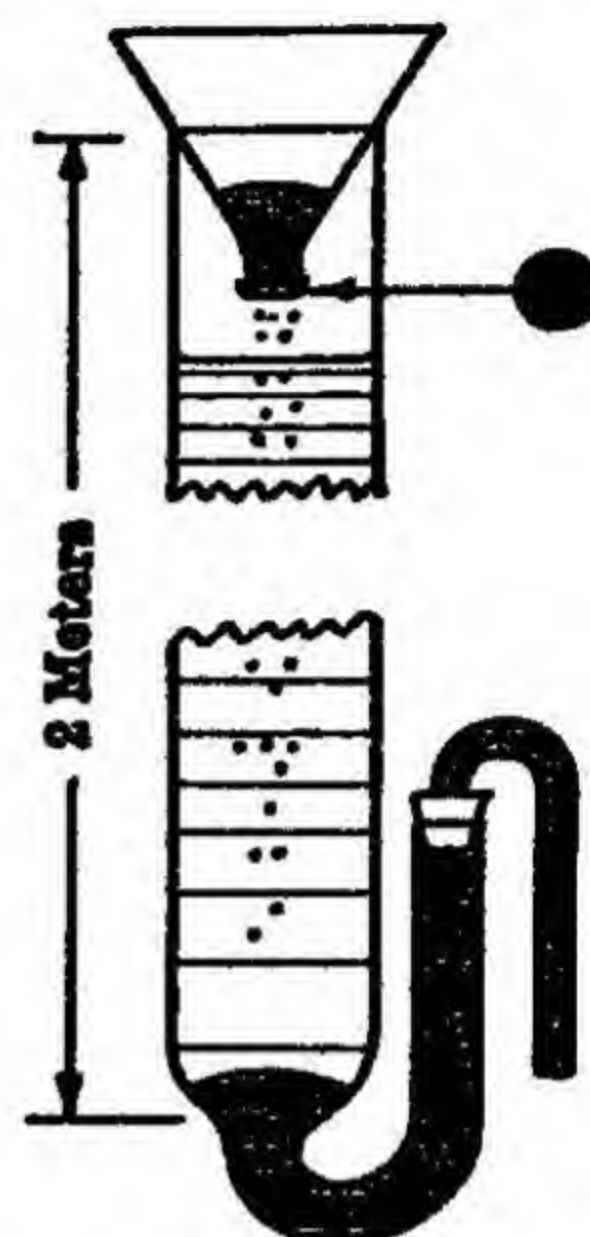


FIG. 62

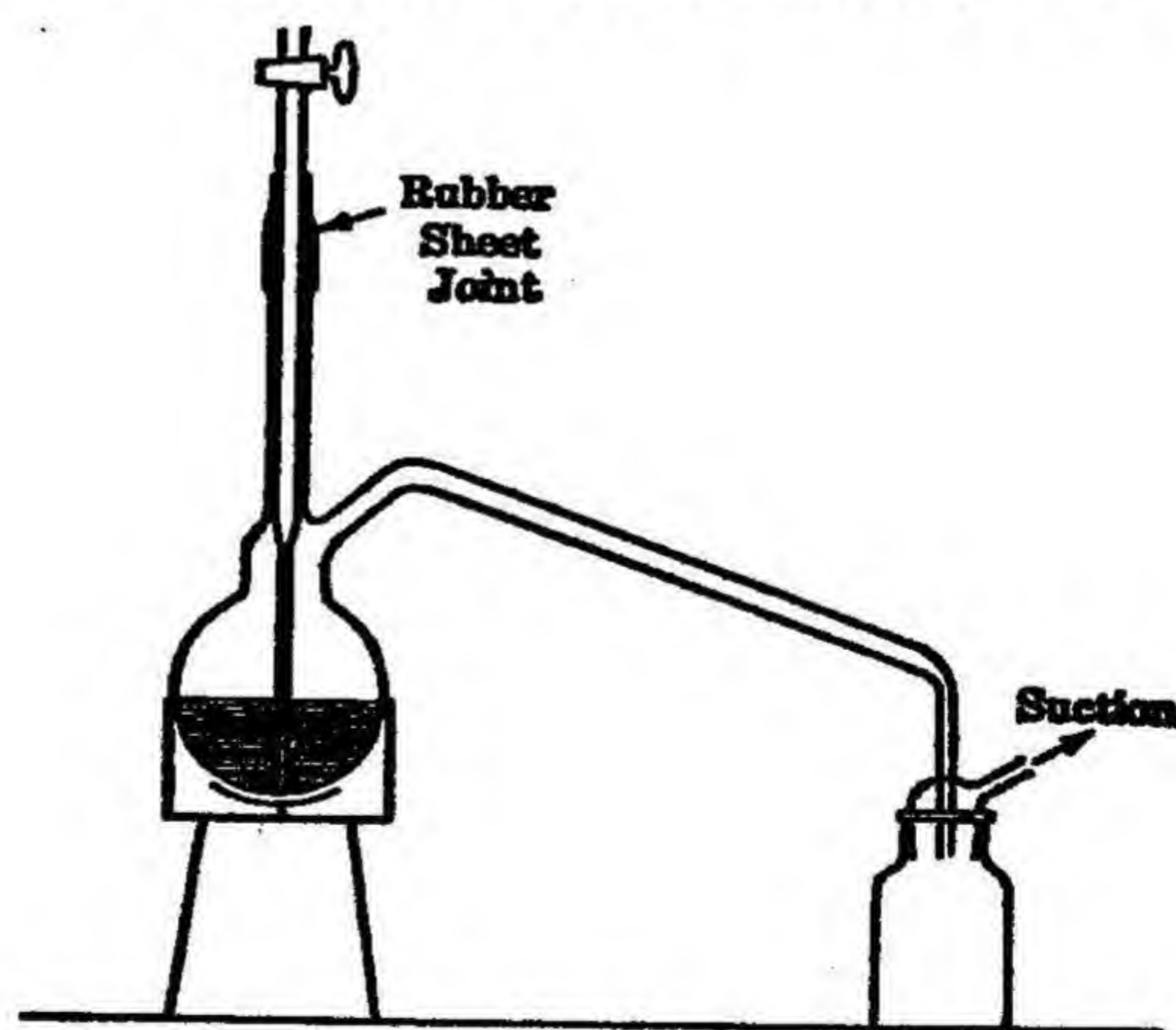


FIG. 63

course.) The oxidation occurs in the gas phase, chiefly. Before the distillate is poured back into the boiler flask for the 2nd and 3rd distillations, the whole apparatus should be thoroughly cleansed of



residual mercury mud and oxidized impurities, by using  $\text{HNO}_3$  and then water, and then drying thoroughly.

With this apparatus 2 or 3 kilograms of pure mercury can be distilled in a few hours. By employment of this method it is probable that mercury can be obtained in a higher degree of purity than can any other known substance.

**Preparation of Cadmium Crystals and Solution.** The following weights (in grams) of cadmium sulfate are dissolved by 100 cc. water at the temperatures indicated.

$^{\circ}\text{C.}$	$\text{CdSO}_4$	$\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$
$0^{\circ}$	75.5	112.5
$15^{\circ}$	76.1	113.4
$25^{\circ}$	76.8	114.7
$40^{\circ}$	78.5	117.9

A saturated solution of commercial cadmium sulfate (prepared with a mechanical stirrer) is filtered into a large crystallizing dish, to a solution layer depth not greater than 1 cm., covered with filter paper and allowed to stand in a place of constant temperature. In a day or so a good crop of beautiful crystals will be obtained. Dry the crystals between filter paper. Now work up 100 cc. of saturated solution from these crystals at room temperature; this will require about 75 cc. water and 86 g. crystals, but a considerable excess of crystals should be used, and the whole stirred over night with a motor-driven stirrer.

**Preparation of Cadmium Amalgam.** Prepare an approximately 12.5% amalgam (for 4 to 6 cells) as follows: Place 90 g. pure mercury in a small crystallizing dish, and place on top of the mercury 31 g.  $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$  crystals and 50 cc. distilled water, made acid with one drop of  $\text{H}_2\text{SO}_4$ . Introduce a platinum loop as anode just beneath the liquid surface; make the mercury the *cathode* with a platinum wire insulated in glass. With a current of 2–3 amperes the cadmium metal deposits in the mercury about as fast as the crystals of  $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$  dissolve. When all the crystals are gone, increase to 4–5 amperes. This ensures the complete deposition of the cadmium, and also generates enough heat to melt the amalgam. While the current is still running,



siphon off the liquid, and at the same time run in a quantity of distilled water, until the current drops to zero. If the amalgam is kept cathode under water it may be left indefinitely with no possibility of oxidation. The amalgam may be melted at any time by adding a little hot water.

**Preparation of Mercurous Sulfate.** "The depolarizer is chiefly responsible for variations in the reproducibility and constancy of standard cells and the preparation of the mercurous sulfate and the making of the paste are still the most difficult and important part of the construction of these standards. . . . It was shown that mercurous sulfate is stable in a sulfuric acid solution when the concentration of the acid is molecular (98 g.  $\text{H}_2\text{SO}_4$  to a liter) or greater, but when the acid strength drops below this value the mercurous sulfate begins to hydrolyze with the formation of a difficultly soluble basic salt,  $\text{Hg}_2(\text{OH})_2 \cdot \text{Hg}_2\text{SO}_4$ ." (Hulett, *Phys. Rev.*, 32, 255-280 (1911).) The following method for the preparation of  $\text{Hg}_2\text{SO}_4$  is taken from Smith, *Trans. Roy. Soc.*, A207, 395 (1908).

In a small evaporating dish treat 100 g. pure mercury with 15 cc. cold conc.  $\text{HNO}_3$ , *under a hood*. When the action has ceased, pour off the mercury and dissolve the crystals ( $\text{HgNO}_3$ ) in 200 cc. dilute  $\text{HNO}_3$  (1 part acid to 40 parts water). Let this solution run from a fine-pointed pipette into 1000 cc. dilute  $\text{H}_2\text{SO}_4$  (1 part acid by weight to 3 parts water). Wash 2 or 3 times with dilute  $\text{H}_2\text{SO}_4$  (1 to 6) by decantation, and filter. If it is not to be used immediately, preserve in a bottle under 1 : 6 dilute  $\text{H}_2\text{SO}_4$ .

**REFERENCES:**

- Taylor, Chaps. VII and XIII.
- Rodebush, Chap. XI.
- Getman and Daniels, Chap. XVII.
- Millard, Chap. XVII.
- Findlay, Chap. XVI.
- Creighton and Fink, *Electro-Chemistry*, Wiley.
- Glasstone, *Electro-Chemistry of Solutions*, Van Nostrand.
- Lehfeldt, *Electro-Chemistry*, Longmans.



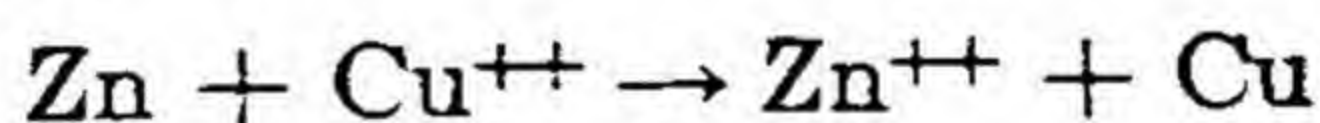
## EXPERIMENT 35

### THE ELECTROMOTIVE FORCE AND THE TEMPERATURE COEFFICIENT OF THE DANIELL CELL

When a galvanic cell, such as the Daniell cell, is allowed to operate "reversibly," that is to say when the electrical energy generated is made to do the maximum amount of work, or if the E.M.F. of the cell is measured with a potentiometer (which is another way of virtually causing the cell to operate reversibly), then the decrease in free energy can be calculated from the relationship

$$-\Delta F = nFE \quad (1)$$

where  $\Delta F$  is the free energy change per gram-ion,  $n$  is the valence of the ion,  $F$  is the faraday (96,490 coulombs), and  $E$  is the E.M.F. of the cell. ( $\Delta$  is pronounced "delta.") For example, in the case of the Daniell cell, where the chemical reaction may be represented as follows



the free energy change per *gram-ion* ( $6.06 \times 10^{23}$  actual ions) of copper displaced, assuming the E.M.F. to be *about* 1.1 volts, would be

$$-\Delta F = 2 \times 96,490 \times 1.10 = 212,278 \text{ volt-coulombs (or Joules).}$$

Dividing by 4.185, the number of volt-coulombs, or of Joules in 1 calorie, we get  $-\Delta F = 50,700$  cal. Also, of course, for 1 *gram equivalent* of chemical change,  $-\Delta F$  would be only 1/2 of 50,700 cal.

This maximum work which can be done in the external circuit, when the galvanic cell is operated reversibly, is by no means necessarily the same as the heat which would be generated,  $-\Delta H$ , when the same chemical reaction is allowed to occur in a calorimeter, although it was at one time supposed that the two were identical. Nor is  $\Delta H$ , the calorimeter heat, to be confused with the heat changes which nearly always do occur in the operation



of any galvanic cell. These latter changes are often referred to as "latent heat" changes, and may be either an evolution of heat (cell tends to warm up during operation), or an absorption of heat from the surroundings (cell tends to cool off during operation), depending on the nature of the cell reaction.

While the heat of the reaction, carried out separately in a calorimeter, and the free energy change in the cell cannot be equated, a relationship connecting the magnitude of these two quantities and also the latent heat is given by the Gibbs-Helmholtz equation (for a derivation of which the student may consult the references at the end of this chapter):

$$\Delta F - \Delta H = T \frac{d(\Delta F)}{dT}.$$

The term on the right-hand side, the absolute temperature multiplied by the rate of variation of the free energy change with temperature, is the latent heat of the cell. Substituting for  $\Delta F$  from Equation 1, and changing sign throughout the equation, we get

$$nFE = -\Delta H + T \cdot nF \frac{dE}{dT}. \quad (2)$$

This equation shows that  $nFE$ , the free energy change, and  $\Delta H$ , the calorimeter heat, would actually be exactly equal, if by any chance  $\frac{dE}{dT}$ , the temperature coefficient of the cell's E.M.F., were exactly zero. When, in any particular cell,  $\frac{dE}{dT}$  is *positive* (E.M.F. gets larger with increasing temperature), then the free energy is larger than the calorimeter heat, and a quantity of latent heat,  $T \cdot nF \frac{dE}{dT}$  is taken by the cell (per gram-ion of chemical change) from the surroundings, when the cell operates. When  $\frac{dE}{dT}$  is *negative*, the free energy is less than the calorimeter heat, and latent heat  $T \cdot nF \frac{dE}{dT}$  is given up to the surroundings.

By means of Equation 2, and with experimental data on the E.M.F. of a cell and the temperature coefficient of the E.M.F., it is obviously possible to calculate  $\Delta H$ , the heat of the reaction in



a calorimeter, and incidentally it may be said that in general a  $\Delta H$  calculated in this way is likely to be a far more reliable value than that actually measured with the usually quite unsatisfactory calorimeter technique. For this calculation, Equation 2 may be rearranged as follows:

$$-\Delta H = \frac{nF}{4.185} \left( E - T \cdot \frac{dE}{dT} \right) \quad (3)$$

**Preparation of Daniell Cells.** Three H-tubes are made similar to those used for the standard cell in Exp. 34 and illustrated in Fig. 60, with the exception that the cross member connecting the two legs contains a two millimeter two-way stop-cock, the bore of which is lightly packed with clean absorbent cotton. In one leg of a well cleaned tube 5 cc. of an approximately 5% copper amalgam are placed and in the other leg an equal amount of an approximately 5% zinc amalgam. The stop-cock is then closed and in the leg containing the zinc amalgam enough  $\text{ZnSO}_4$  solution is added to bring the level of the solution to about 3 cm. above the cross member of the tube. A quantity of  $\text{CuSO}_4$  solution is then added to the other leg so as to equalize the levels in both legs. In this filling operation care should be taken to see that air bubbles do not collect about the stop-cock and prevent the two solutions from coming into contact with each other. The solutions should be carefully prepared from pure  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and pure  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  so as to contain 1 mol of  $\text{CuSO}_4$  per 100 mols of  $\text{H}_2\text{O}$  and 1 mol of  $\text{ZnSO}_4$  per 100 mols of  $\text{H}_2\text{O}$ . External connections are made through the amalgams by means of leads made from small glass tubing, with a platinum wire sealed in one end, and filled with mercury in which a copper wire is inserted. The leads are supported by a one-hole rubber stopper fitted into the opening of the legs. The stoppers are necessary to prevent concentration changes due to evaporation and should be sealed with paraffin or de Khotinsky cement so as to be water tight.

The use of *amalgams* is necessary because of the lack of reproducibility of the cells when metallic zinc and copper electrodes are used. The concentration of the amalgams may be varied from about 2-15% without producing appreciable changes in the E.M.F. of the cells.

The amalgams may be prepared electrochemically in much the



same way as the Cd amalgam was prepared for the standard cell in Exp. 34. A weighed quantity of carefully purified Hg is placed in a small crystallizing dish into which is poured a molar solution of  $\text{ZnSO}_4$ . The Hg is made the cathode with a platinum wire insulated in glass and the anode is a strip of pure electrolytic zinc. A similar cell containing a molar solution of  $\text{CuSO}_4$  and an anode of pure electrolytic copper is set up and the two cells are connected in series. Enough electricity as indicated by an ammeter and a watch is passed through the cells to produce amalgams of the required concentration.

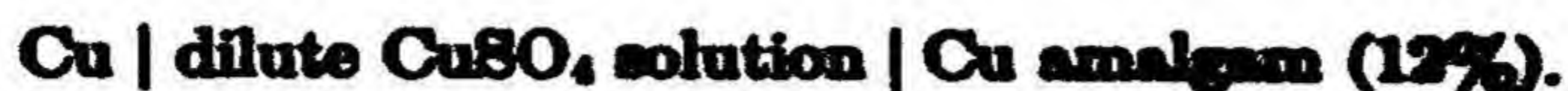
Three Daniell cells prepared as described above are placed in a thermostat at  $25^\circ \text{C}$ . When a constant temperature has been attained their electromotive forces are measured with a suitable potentiometer reading to 0.1 of a millivolt. The measurements are repeated in about an hour and if in agreement with the first measurements, the cells are then placed in an ice-bath and their electromotive forces are again measured at or about  $0^\circ \text{C}$ ., after they have attained this temperature. In making these measurements care should be taken to see that the stop-cocks are open only during the actual measurement, otherwise diffusion may affect the reproducibility of the results.

From the electromotive force of the Daniell cells at the two temperatures calculate the temperature coefficient  $\frac{dE}{dT}$  of the E.M.F. of the cell. Then using this value and the measured E.M.F. of the cell calculate by means of Equation 3, the calorimeter heat of reaction at  $25^\circ \text{C}$ . Compare this value with that determined calorimetrically for the same reaction in Exp. 20. How do you account for such differences as you may find? Are the predictions, made by Equation 2, concerning the relationship between the free energy and calorimeter heat when  $\frac{dE}{dT}$  is negative, borne out by your measurements?

In order to make a proper comparison between the calorimeter heat determined in Exp. 20, and the calorimeter heat calculated here, we should, of course, have set up a Daniell cell using pure metallic Cu and Zn as electrodes. We were compelled to use amalgams for the sake of reproducibility. The heat of amalgamation of Zn is practically zero; that of Cu is about 825 cal., calcu-



lated from the E.M.F. and the temperature coefficient of the following cell:



A thorough study of the Daniell cell has been made by Cohen, Chattaway and Tombrock, *Z. phys. Chem.*, 60, 706 (1907) and this work should be consulted in connection with this experiment.

**REFERENCES:**

- Taylor, Chaps. VII and XIII.
- Rodebush, Chaps. V and XI.
- Getman and Daniels, Chaps. VI and XVII.
- Millard, Chap. XVII.
- Findlay, Chaps. XIV and XVI.
- Newman's *Electrolytic Conduction*, Chap. VI.
- Glasstone's *Electrochemistry of Solutions*, Chap. XIII.



## EXPERIMENT 36

### NORMAL ELECTRODE POTENTIALS

The potential difference resulting from the contact of a metal with a solution of its own ions (Exp. 34) is due according to the theory of Nernst to the equilibrium established between two opposing forces. One of these forces is manifested by the tendency of the metal to send ions into the solution in opposition to the other which tends to deposit metal ions from the solution upon the metal. The magnitude of the former force is expressible in terms of the "electrolytic solution pressure" of the metal (a hypothetical concept) and the latter in terms of the osmotic pressure of the metal ions of the solution which in turn is proportional to the ionic activity. The electromotive force developed at such a metal-solution junction is given by the Nernst equation

$$E = \frac{RT}{nF} \ln \frac{k[C]}{P} \quad (1)$$

in which  $k$  is a constant for a given metal;  $[C]$  is the concentration of the metal ions in the solution;  $P$  is the electrolytic solution pressure of the metal; and the remaining terms have their usual significance.

Since for a given metal at constant temperature the electrolytic solution pressure may be regarded as constant it is evident from equation (1) that the single electrode potential of a metal is dependent upon the concentration of the metal ions in which it is immersed. In order therefore to provide a uniform basis of comparison of such potentials it is necessary to select some one ionic concentration as a standard. The standard chosen is 1 gram-ion per 1000 grams of solvent. Expressed in terms of the "activity concept" the normal or standard electrode potential  $E_0$  is the potential of a metal when in contact with a solution of its own ions at unit activity. The normal electrode potential may be calculated from the single electrode potential  $E$  measured at some activity other than unity by the following equation

$$E_0 = E - \frac{RT}{nF} \ln a_+ \quad (2)$$

in which  $a_+$  is the activity of the metal ion.



DETERMINATION OF THE NORMAL ELECTRODE POTENTIALS  
OF LEAD, ZINC, COPPER AND SILVER

Normal electrode potentials are usually determined by measuring the E.M.F. of a cell consisting of the metal immersed in a solution of its ions combined with a calomel or hydrogen reference electrode. The E.M.F. of such a cell is the single electrode potential difference of the metal-solution interface referred to the calomel or hydrogen electrode as zero, together with any added potential differences due to liquid-liquid junctions within the cell. The liquid-liquid junction potentials may be disposed of either by calculating their values and correcting the measured potentials or by reducing them to such small values that they may be safely neglected. In this instance the latter procedure will be followed by interposing a salt bridge of 3 *N*  $\text{NH}_4\text{NO}_3$  solution between the KCl electrolyte of the calomel cell and the metal ion solution of the electrode whose potential is being determined.

The normal calomel electrode is used as a reference electrode and the arrangement of the cells is the same as in Fig. 64, Exp. 37, except that the hydrogen electrode is replaced by the metal electrode in contact with its solution and a 50 cc. beaker containing 3 *N*  $\text{NH}_4\text{NO}_3$  solution is substituted for the large beaker shown in the figure. The metals and their solutions are placed in electrode holders of the type shown in Fig. 59, Exp. 33. The cell circuit is completed by dipping the goose neck of the electrode holder beneath the surface of the 3 *N*  $\text{NH}_4\text{NO}_3$  solution in the small beaker having previously filled the bridge with this same solution. The cell is then connected to a potentiometer and its E.M.F. is measured as described in Exp. 34.

Pure sheet lead cut into narrow strips and thoroughly cleaned in HCl solution and distilled water are used for the lead electrodes. The silver electrodes are prepared by electrolytically depositing silver upon narrow strips of sheet silver. The copper and zinc amalgams prepared in Exp. 35 may be used for the copper and zinc electrodes. The electrolyte solutions are 0.1 *M*  $\text{AgNO}_3$ ;  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{CuSO}_4$  and  $\text{ZnSO}_4$ . Two electrodes of each metal are prepared and the single electrode potential of each referred to the normal calomel electrode as zero is measured in both 0.1 *M* and 0.01 *M* concentrations of the corresponding electrolyte. From



these measured values calculate the normal electrode potentials of the metals by means of Equation (2).

For these calculations use the following activity coefficients at 25° C.

	0.01 M	0.1 M
CuSO <sub>4</sub>	0.404	0.158
ZnSO <sub>4</sub>	0.400	0.161
AgNO <sub>3</sub>	0.902	0.723
Pb(NO <sub>3</sub> ) <sub>2</sub>	0.692	0.367

Compare the values obtained with the accepted values for the normal electrode potentials of these metals referred to the normal calomel electrode as zero.

## REFERENCES:

- Taylor, Chap. XIII.
- Rodebush, Chap. XI.
- Getman and Daniels, Chap. XVII.
- Millard, Chap. XVII.
- Newman, *Electrolytic Conduction*, Chap. VI.
- Glasstone, *Electrochemistry of Solutions*, Chap. XIV.



## EXPERIMENT 37

### THE HYDROGEN ELECTRODE

Before doing this experiment it is advisable that the student should have performed Exp. 34.

A knowledge of the concentration of the hydrogen ions in aqueous solutions is of considerable theoretical and technical importance. Thus, for example, it is frequently possible to control the course of a given reaction by varying the hydrogen ion concentration. Numerous analytical procedures make use of the sharp changes in hydrogen ion concentration accompanying certain reactions. One of the most satisfactory ways of determining hydrogen ion concentration is the electromotive force method. This method takes advantage of the fact that a platinized platinum electrode saturated with hydrogen and immersed in an aqueous solution behaves not as a platinum electrode but as a hydrogen electrode. That is, there is an equilibrium established between the tendency for hydrogen ions to be sent into the solution, or the electrolytic solution pressure of the hydrogen, and the tendency for hydrogen ions to be discharged on the electrode, or the osmotic pressure of the ions in the solution. There is thus established a potential difference between the solution and the electrode, the value of which is dependent (at a given pressure of the hydrogen gas used to saturate the electrode) upon the concentration of the hydrogen ions in the solution. The value of this potential may be experimentally determined by measuring the electromotive force of a voltaic cell composed of the hydrogen electrode and a calomel electrode of known potential.

Before giving the details of the method, the equilibrium established between water and its ions will be considered. The equation representing the ionization of water, and the recombination of the ions is



The equilibrium relationship between the activities\* of these

\* The expression "activity" will be used throughout this chapter instead of "concentration"; although when the concentration is less than 0.001 molal, the activity coefficient may be taken as 1, and the activity and concentration are the same.



substances is expressed, in accordance with the mass action law, by the equation

$$\frac{a_{\text{H}^+} \times a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} = K' \quad (2)$$

in which  $K'$  is the equilibrium constant and  $a_{\text{H}^+}$ ,  $a_{\text{OH}^-}$ , and  $a_{\text{H}_2\text{O}}$  are the activities. Due to the slight ionization of the water the activity of the non-ionized molecules is very great in comparison with the activities of the ions, and can therefore be considered as constant. Equation 2 may then be written as

$$a_{\text{H}^+} \times a_{\text{OH}^-} = K_{\text{H}_2\text{O}}. \quad (3)$$

The value of this ionization constant  $K$  at about room temperature is  $1 \times 10^{-14}$ . Since hydrogen and hydroxyl ions are present in equivalent quantities it follows that the activity of each is  $1 \times 10^{-7}$ . If acid is added to pure water the activity of  $\text{H}^+$ ,  $a_{\text{H}^+}$ , is increased or if alkali is added the activity of  $\text{OH}^-$ ,  $a_{\text{OH}^-}$ , is increased and as one increases the other decreases. This is in consequence of the relationship expressed in Equation 3 which requires that the product of the two ion activities remain equal to  $1 \times 10^{-14}$ . Thus if enough alkali is added to water to increase  $a_{\text{OH}^-}$  from  $1 \times 10^{-7}$  to  $1 \times 10^{-3}$ ,  $a_{\text{H}^+}$  must change to  $1 \times 10^{-11}$ .

$$a_{\text{H}^+} = \frac{K_{\text{H}_2\text{O}}}{a_{\text{OH}^-}} = \frac{10^{-14}}{10^{-3}} = 10^{-11}.$$

It is evident from this relationship that the algebraic sum of the exponents of 10 for  $a_{\text{H}^+}$  and  $a_{\text{OH}^-}$  must always be  $-14$ , at this temperature.

Instead of expressing  $a_{\text{H}^+}$  in terms of gram-ions per liter the "hydrogen-ion-exponent" or pH value is frequently used. If the  $a_{\text{H}^+}$  is expressed as a power of 10, the exponent with its sign changed is defined as the pH value, that is,  $a_{\text{H}^+} = 10^{-\text{pH}}$  or  $\text{pH} = \log \frac{1}{a_{\text{H}^+}} = -\log a_{\text{H}^+}$ . For a solution having an  $a_{\text{H}^+}$  of  $1 \times 10^{-4}$  the  $\text{pH} = 4$ , and for an  $a_{\text{H}^+}$  of  $1 \times 10^{-6}$  the  $\text{pH} = 6$ , etc. While the pH values are apparent from simple inspection in these cases, it frequently happens that the negative exponent has to be determined from a table of Briggsian or common logarithms. Thus in a solution having an  $a_{\text{H}^+}$  of  $5 \times 10^{-4}$  the negative exponent of 10 is obtained as follows. The logarithm of



5 is 0.699. This, when added algebraically to  $-4$ , gives a value  $-4 + 0.699 = -3.301$  for the exponent (i.e., for  $\log_{10} 5 \times 10^{-4}$ , perhaps more commonly written as  $6.699 - 10$ ) or a pH value of 3.301. While the pH system of notation is less cumbersome than the  $a_{H^+}$  system, it nevertheless possesses some disadvantages. One of these, pointed out by W. M. Bayliss in *Principles of General Physiology*, p. 184, is that unless one is accustomed to thinking in exponential terms, rather marked differences in concentration are not self-evident from the pH values. For example, while it is perfectly obvious that an  $a_{H^+}$  of  $6 \times 10^{-4}$  is twice that of  $3 \times 10^{-4}$ , this fact is not so apparent from their pH values of 3.222 and 3.523.

The absolute potential of the hydrogen electrode (saturated with hydrogen gas at a pressure of 1 atmosphere) in a solution normal with respect to the hydrogen ion is  $+0.282$  volt at  $25^\circ \text{C.}$ ; that is, the osmotic pressure of the hydrogen ions in the solution is greater than the electrolytic solution pressure of the hydrogen electrode and therefore hydrogen ions discharge on the electrode. As the concentration of hydrogen ions decreases the osmotic pressure decreases and may finally become less than the electrolytic solution pressure. In this event the potential would then change from a positive to a negative value.

As has already been pointed out, the calomel electrode (with  $N$  KCl solution) is used as the reference electrode in the measurement of the potential of the hydrogen electrode. It has an absolute value of  $+0.565$  volt at  $25^\circ \text{C.}$ , which when referred to the normal hydrogen electrode as zero becomes  $+0.283$  volt. The cell formed from these electrodes may be represented as follows: (See Exp. 34, on standard cell.)

$\text{H}_2$  electrode |  $\text{H}^+$  solution | Saturated KCl |  $N$  KCl,  $\text{HgCl}$  |  $\text{Hg}$ .

The Nernst equation

$$E = 0.059 \log \frac{1}{a_{H^+}} + 0.283 \quad (4)$$

expresses the relation between the hydrogen ion activity,  $a_{H^+}$ , and the measured electromotive force  $E$  of the cell.

Figure 64 shows the arrangement of the electrodes. The solution whose hydrogen ion concentration is to be measured is placed in the beaker D and in this solution the hydrogen electrode is immersed. The calomel electrode dips into a small vessel G



containing a saturated potassium chloride solution. The vessel G and the beaker D are connected by means of a siphon filled with saturated potassium chloride solution. The purpose of this is (1) to reduce as far as possible the liquid junction potentials and (2) to prevent variations in the calomel electrode resulting from the diffusion of the solution D into the calomel cell, which would likely occur if it were immersed directly in D. Pure hydrogen passes into the electrode holder at its top ( $H_2$ ) and over the platinized platinum plate F. When the electrode and solution become saturated the electromotive force of the cell is measured with a potentiometer as described in the standard cell experiment (Exp. 34). Why is it necessary in this case to use a null method?

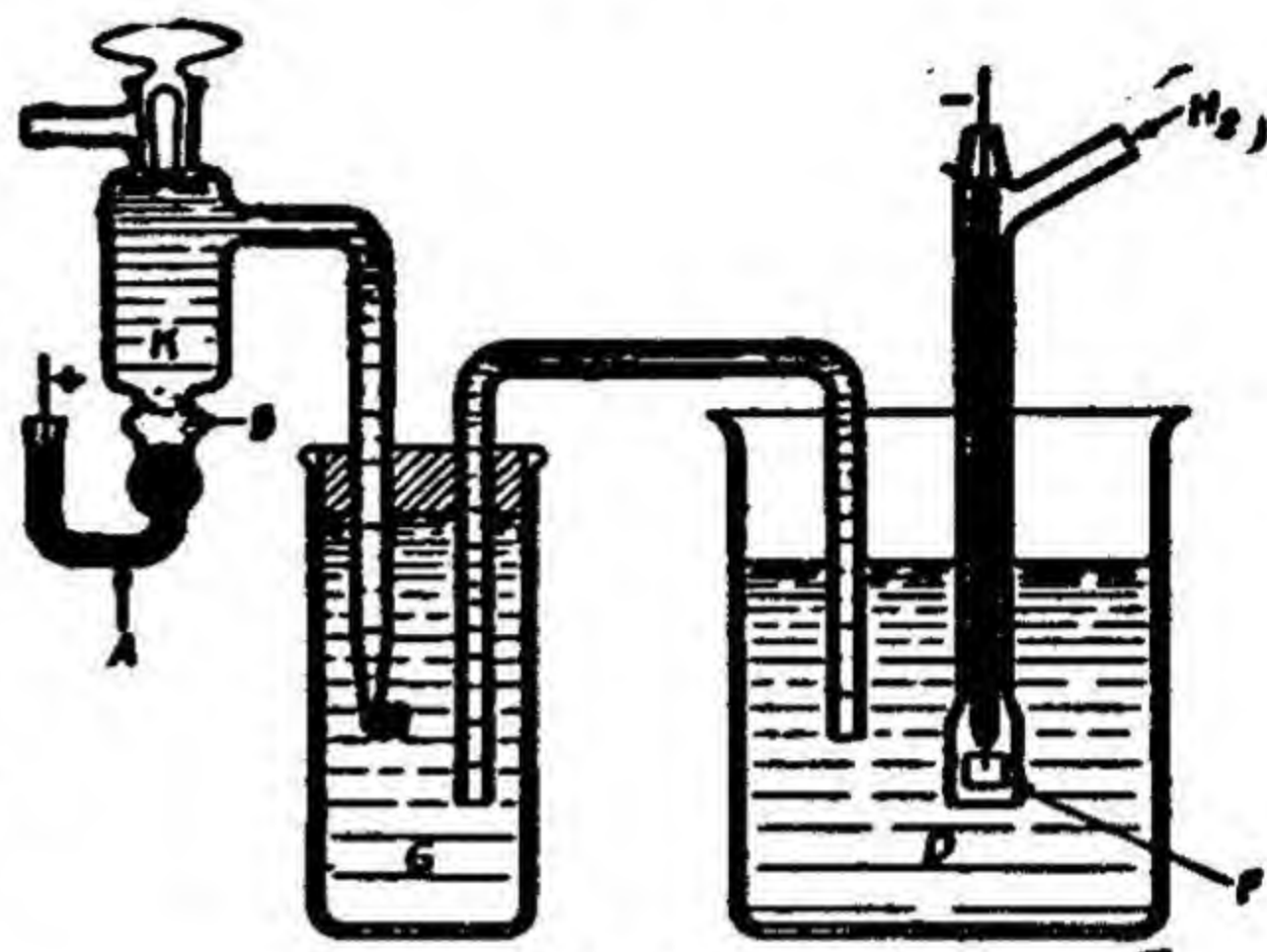


FIG. 64

The calomel electrode is prepared as follows. Redistilled mercury, A, is placed in the glass cell as indicated in the figure. The mercury is covered with a layer of pure calomel B, made into a paste with a *normal* potassium chloride solution. (The calomel may be prepared in the same way as  $Hg_2SO_4$  in Exp. 34, except that  $HCl$  is used instead of  $H_2SO_4$ . The final product,  $HgCl$ , should be very thoroughly washed with distilled water.) The remainder of the cell is filled with a normal potassium chloride solution prepared from pure recrystallized potassium chloride. The lead wire immersed in the mercury should be of platinum; convenient and economical leads are described in the experiment on the cadmium standard cell.

If a normal hydrogen electrode, dipping into a  $H^+$  solution of  $a = 1$ , were used instead of the calomel electrode, Equation 4, without the term 0.283, would apply. The point is that it is much more convenient to use the calomel electrode. The mercury, because of its very low solution pressure, takes on a positive charge in the presence of  $Hg^+$  in the  $KCl$  solution saturated with calomel ( $HgCl$ ). The calomel also acts as a *depolarizer*. In the absence of calomel, hydrogen would be deposited on the  $Hg$  surface,



when the cell functions, since electrons run through the external electrical connecting system from the negative H-electrode on to the mercury electrode. A film of hydrogen gas would form which would insulate the Hg surface from the solution, or *polarize* the Hg surface, as we say. Actually, however, in the presence of the calomel,  $\text{Hg}^+$  ions are deposited as Hg atoms on the surface, and these are absorbed into the mass of Hg, and no polarizing film forms.

The hydrogen electrode is constructed as shown in the figure. F is a piece of platinum foil about a centimeter square fastened to a platinum wire sealed into the capillary tube containing a little mercury and into which the lead (—) is inserted. This platinum plate is covered with platinum black (see Exp. 31, on electrical conductivity). Exit holes are provided for the hydrogen gas near F so that the platinum foil is about half immersed in the liquid. The hydrogen should be pure. The most convenient source is compressed *electrolytic* hydrogen contained in a steel cylinder. For most work this can be used without purification; however, when necessary it may be purified by passing the gas over potassium hydroxide sticks and through a tube of red hot platinized asbestos. The hydrogen should escape through the holes in the glass jacket at a rate of two or three bubbles a second.

Before proceeding with the following determinations, read the article by Hildebrand, *J. Am. Chem. Soc.* **35**, 847 (1913).

#### (A) TITRATION OF A STRONG ACID WITH A STRONG BASE

Prepare 0.5 *N* solutions of hydrochloric acid and sodium hydroxide. Saturate a hydrogen electrode by passing hydrogen over it in distilled water for about 15 minutes. Then put about 20 cc. of the acid solution in a 250 cc. beaker and add enough distilled water to fill the beaker about half-full. Into this solution put the hydrogen electrode and the siphon from the calomel electrode. Pass hydrogen over the electrode, connect the cell to a potentiometer and measure the potential. After a five-minute interval again measure the potential and if it has remained constant the determination can be proceeded with; if not, wait until a constant value is obtained. Then add from a burette some of the sodium hydroxide solution, a few cubic centimeters at a time at first. Measure the potential after each addition, making sure that it is



constant before adding more base. When the potential begins to change considerably with small additions of the base, decrease the quantity added to a drop at a time as the neutral point is approached. It is well to have a little phenolphthalein present in the solution to indicate the neutral zone. When the neutral point has been passed the base can again be added in larger amounts, until the solution is strongly basic. From the measured potentials calculate the hydrogen ion concentration and also the pH values. Plot the potentials as ordinates against the number of cubic centimeters of the base added as abscissas and draw the curve. On the right hand side of this graph plot the  $a_{H^+}$  values as ordinates so that both potential and  $a_{H^+}$  may be read from the curve. What part of the curve corresponds to the neutral point? How does the "end point" obtained for the curve compare with that actually required by the quantity of acid titrated? Does this agree with the "end point" indicated by the phenolphthalein?

#### (B) TITRATION OF A WEAK ACID WITH A STRONG BASE

Prepare a 0.5 *N* acetic acid solution and titrate this with the 0.5 *N* sodium hydroxide, following the same procedure as in (A) except that at the beginning of the titration smaller quantities of the base are added. This is to avoid missing the first inflection in the curve which occurs in the neighborhood of 0.4 volt. Complete the titration, and, as before, plot the potentials and  $a_{H^+}$  values against the number of cubic centimeters of base added. Interpret this curve in the light of the chemistry of the reactions involved in the titration.

#### (C) TITRATION OF SODIUM CARBONATE WITH HYDROCHLORIC ACID

Prepare a 0.5 *N* sodium carbonate solution and titrate this with the 0.5 *N* hydrochloric acid solution, following the same procedure as in (A) except that phenolphthalein is added to the carbonate solution to indicate the change from carbonate to acid carbonate. Note the point in the titration at which this occurs. When the color disappears, add methyl orange and proceed with the titration, noting the point at which this indicator changes color. Plot the curves as before and on the basis of your results justify the use of the indicators selected for this titration.



(D) DETERMINATION OF MAGNESIUM OXIDE IN THE  
PRESENCE OF CALCIUM OXIDE

In the usual analytical procedure for this determination it is necessary to remove the calcium before determining the magnesium. This separation can be avoided by the use of the hydrogen electrode in the method devised by Hildebrand. The principle involved may be briefly stated as follows. Because of its smaller solubility, magnesium hydroxide is precipitated before calcium hydroxide when sodium hydroxide is added to a solution containing calcium and magnesium ions. In such a solution, then, the concentration of the hydroxyl ions can not be appreciably increased so long as magnesium ions are present. However, when all of the latter have been removed by precipitation as magnesium hydroxide, the concentration can then be increased up to the value required for the precipitation of the calcium ions. If these hydroxyl ion concentration changes (in terms of hydrogen ions) are followed by means of the hydrogen electrode, a curve can be constructed by plotting the potentials against the number of cubic centimeters of sodium hydroxide added. From the inflections in the curve corresponding to the beginning and to the end of the precipitation of the magnesium hydroxide, the number of cubic centimeters of standard sodium hydroxide required can be determined and from this the quantity of magnesium hydroxide precipitated can be calculated.

The following procedure is quoted directly from the article of Hildebrand, previously referred to. Secure from the instructor an "unknown" containing magnesium and calcium and determine the per cent of  $\text{MgO}$ .

"To carry out a determination, the sample, say of limestone, is first weighed out, the quantity depending upon the magnesia content and the accuracy desired. The end point of the titration can be determined to about 0.2 cc., using normal alkali, which corresponds to 0.004 gram  $\text{MgO}$ . Therefore, a sample containing about 0.4 gram  $\text{MgO}$ , and requiring 20 cc. for its precipitation, could have its magnesia content determined with an accuracy of about 1 part per 100. Greater accuracy is, of course, offset by slightly greater time, so that the amount of the sample must be determined according to the conditions.



"The sample having been weighed out, with an accuracy of 1 part per 100, it is transferred to a small round-bottomed flask, sufficient dilute hydrochloric acid added to effect its solution, and the last traces of carbon dioxide expelled by boiling for a moment under reduced pressure by the aid of a filter pump. A safety trap should be inserted between the flask and the pump. As soon as the solution of the sample is complete and the carbon dioxide expelled, the contents of the flask are washed out into a beaker for titration. The gang does not interfere and need not be filtered out.

"The hydrogen electrode and the siphon of the calomel electrode are next inserted into the solution, and the titration begun. Time is saved if the hydrogen electrode has been previously saturated while dipping into distilled water. A moment is necessary for the readings to become constant due to the contact of the electrode with the air in transference. The normal alkali, free from carbonate, is added until the e.m.f. begins to rise. The neutralization of the excess of hydrochloric acid may be quickly effected if methyl-orange is present and the alkali added until it just turns yellow. This will indicate the beginning of the rapid rise in the curve, before which e.m.f. readings are unnecessary. The readings of e.m.f. from now on should be plotted directly as they are taken on cross-section paper. The parts of the curve to be observed carefully are the end of the first rise and the final rise from the precipitation of magnesium hydroxide to that of calcium hydroxide. Along this portion readings should be taken every 0.2 cc. The point of inflection of the smooth curve drawn through these points is taken as the end of the reaction."

#### (E) DETERMINATION OF pH AT WHICH INDICATORS CHANGE COLOR

Following the procedure given in (A), titrate 20 cc. of 0.5 *N* HCl, diluted with distilled water, with 0.5 *N* NaOH in the presence of the indicators used in Exp. 38, and in addition use alizarin, litmus and phenolphthalein. Determine the pH value at which the color change occurs for each indicator used.



## (F) EFFECT OF HYDROGEN GAS PRESSURE ON E.M.F.

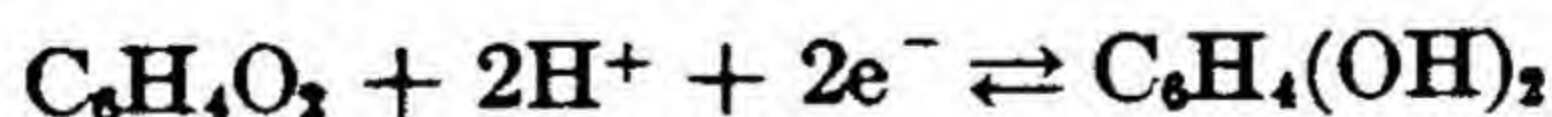
As we have already suggested on a previous page, the potential at a hydrogen electrode depends to some extent on the hydrogen gas pressure at which the electrode is saturated. The difference in electrode potential between an electrode saturated at 760 mm. and, say, at 740 mm. (both of course immersed in a solution of the same  $a_{H^+}$ ) is given by the equation,

$$E_{760} - E_{740} = \frac{RT}{2F} \ln \frac{760}{740}$$

Will the electrode potential become more or less positive with decreasing gas pressure? This correction must be made in accurate work, as well as a correction for hydrostatic pressure, if the hydrogen escapes from the electrode by bubbling, as in the present experiment. Correction must also be made for the aqueous tension of the water, since the hydrogen is not dry but saturated with water vapor. The point, of course, is that the value 0.282 volt at 25° is the potential of the electrode dipping into a normal solution of  $H^+$ , when the hydrogen gas pressure is really 760 mm. The student should calculate all of these corrections for himself and determine whether they are large enough to be justified in the present situation, i.e., whether they lie inside or outside of his other unavoidable experimental errors.

## (G) THE QUINHYDRONE ELECTRODE

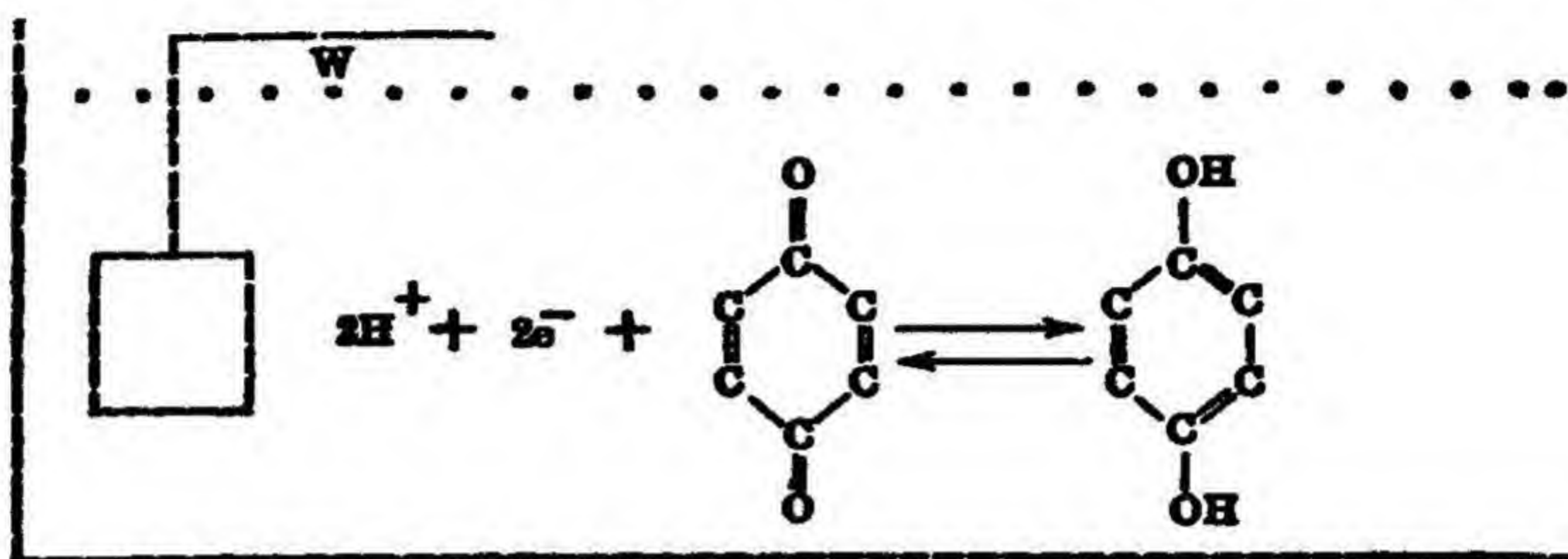
Hydrogen ion concentrations, or activities, may also be determined by means of the *quinhydrone electrode*. Quinhydrone is an equi-molecular mixture of hydroquinone,  $C_6H_4(OH)_2$  and quinone,  $C_6H_4O_2$ . The reversible reduction of quinone (and oxidation of hydroquinone) may be represented by the equation



where  $e^-$  is an electron. If a platinum or gold electrode (wire or plate) is dipped into an aqueous solution of quinhydrone (generally 0.05  $M$ ), and  $H^+$  introduced by adding an acid, the equilibrium is disturbed (reaction goes to right) and a new equilibrium is established. The only source of electrons, which permit the reaction to proceed to the right where  $H^+$  ions are added, is the



platinum electrode, and the rest of the electrical system to which it is connected through the wire W. Electrons are sucked off this electrode into the solution to take part in the reaction, so that the electrode becomes positively charged as far as the metallic wire W and the rest of the system (say a calomel half-cell) are concerned. On the other hand, if  $\text{OH}^-$  ions are introduced into the



solution, the  $\text{H}^+$  ions are used up to form water and the quinhydrone reaction goes to the left, forming quinone and liberating electrons. These electrons are taken up by the platinum electrode which thereby tends to become more negatively charged. Thus the action is virtually the same as with the hydrogen electrode. It will be recalled that in that case also, increasing  $\text{H}^+$  activity in the solution tended to make the hydrogen electrode more positive, because of the increasing osmotic pressure of  $\text{H}^+$ ; whereas decreasing  $\text{H}^+$  activity made the hydrogen electrode more negative.

If a half-cell of quinhydrone electrode containing a *normal* (1.0 *N*) activity of  $\text{H}^+$  is connected to a half-cell of hydrogen electrode dipping into a *normal*  $\text{H}^+$  solution, the E.M.F. of the complete cell can be shown experimentally to be 0.699 volt. This is a characteristic constant of this system, and we shall designate it as  $E_0$ . Now, if the activity of  $\text{H}^+$  is either increased or decreased in the quinhydrone half-cell, the E.M.F. is given by the equation

$$E = E_0 - \frac{RT}{2F} \ln \frac{a_{\text{C}_6\text{H}_4\text{O}_2}}{a_{\text{C}_6\text{H}_4(\text{OH})_2} \cdot a_{\text{H}^+}^2} \quad (5)$$

But since in the equi-molecular mixture, quinhydrone,  $a_{\text{C}_6\text{H}_4\text{O}_2} = a_{\text{C}_6\text{H}_4(\text{OH})_2}$ , this equation reduces to the form

$$E = E_0 - \frac{RT}{2F} \ln \frac{1}{a_{\text{H}^+}^2} \quad \text{or} \quad E = E_0 + \frac{RT}{F} \ln a_{\text{H}^+}$$



or at 25°,

$$E = 0.6990 + \frac{2.303 \times 8.315 \text{ (volt-coulombs)} \times 298}{96,500} \log a_{\text{H}^+}$$

or

$$E = 0.6990 + 0.059 \log a_{\text{H}^+}. \quad (6)$$

Thus, since under these conditions, the quinhydrone electrode is more positive than the normal hydrogen electrode, an increase in  $a_{\text{H}^+}$  in the quinhydrone solution would mean an increase in  $E$ , which bears out our previous statement. With this equation, one can calculate quantitatively the  $a_{\text{H}^+}$  (in the quinhydrone solution) from the potentiometric measurement of the E.M.F. of this cell. Ordinarily, instead of using a normal hydrogen electrode as the other half cell, one employs a calomel electrode, that dips into the quinhydrone solution. If a  $N$  KCl calomel electrode is used, with an absolute potential of  $+0.565$  volt at 25°, then since this is  $0.283$  volt more positive than the normal hydrogen electrode ( $+0.282$  volt),  $E_0$  in Equation 6 becomes  $0.699 - 0.283 = 0.416$  volt.

The quinhydrone electrode cannot be used in alkaline solutions having a pH greater than about 8, both because of the rapid oxidation of the organic molecules by oxygen from the air in alkaline solution, and also because at a pH of about 8, the hydroquinone becomes appreciably ionized, and Equation 5, above, cannot be applied. There are also other limitations. One of the principal advantages of the quinhydrone electrode is the rapid attainment of equilibrium, as compared with the usual 15 or 20 minute delay encountered in waiting for the hydrogen electrode to reach steady values.

#### REFERENCES:

- Taylor, Chaps. XII and XIII.
- Rodebush, Chaps. IX and XI.
- Getman and Daniels, Chap. XVII.
- Millard, Chaps. VIII and XVII.
- Findlay, Chap. XVI.
- Clark, *The Determination of Hydrogen Ions*.
- Glasstone's *Electrochemistry of Solutions*, Chap. XVI.
- Newman, *Electrolytic Conduction*, Chap. VI.



## EXPERIMENT 38

### (A) BUFFER SOLUTIONS AND INDICATOR COLOR SCALE; (B) DEGREE OF HYDROLYSIS; (C) IONIZATION AND CHEMICAL CONSTITUTION

In the case of a strong electrolyte the actual degree of ionization is undoubtedly 100%. But the effectiveness of the individual ions is to some extent diminished by the forces of electrostatic attraction between the  $+$  and  $-$  ions. From this viewpoint, instead of thinking in terms of the old Arrhenius "degree of ionization," it is in many ways more useful and satisfactory to deal with the ion population in terms of "activity" and "activity coefficient." It is well known that the equilibrium equation when applied to a reaction involving a strong electrolyte, such as



namely

$$\frac{c_{A^+} \cdot c_{B^-}}{c_{AB} \text{ (in solution)}} = K$$

does not work, i.e., it does not give constant values for  $K$ , the ionization constant, when we attempt to use some suitable means for calculating  $c_{A^+}$ ,  $c_{B^-}$ , and  $c_{AB}$  by measuring the "degree of ionization." The activity of  $A^+$  and of  $B^-$  and of  $AB$  may be defined as that function of  $A^+$  and of  $B^-$  and of  $AB$  which will make this equilibrium equation work; and the "activity coefficients,"  $\gamma_{A^+}$ ,  $\gamma_{B^-}$  and  $\gamma_{AB}$ , are the factors by which the concentrations must be multiplied to give the activities. (See Rodeshush, Chap. IX, for a discussion of activity and activity coefficient.)

The student must not, however, get the idea that "activity" and "activity coefficient" are mere mathematical fictions. These functions can be evaluated experimentally from freezing-point lowerings, vapor pressure data, and in other ways. In this chapter we shall represent activity by the symbol ( ); thus the activity of  $H^+$  will be written  $(H^+)$ . In the case of *weak* electrolytes, however, it is still useful to think in terms of degree of ionization,

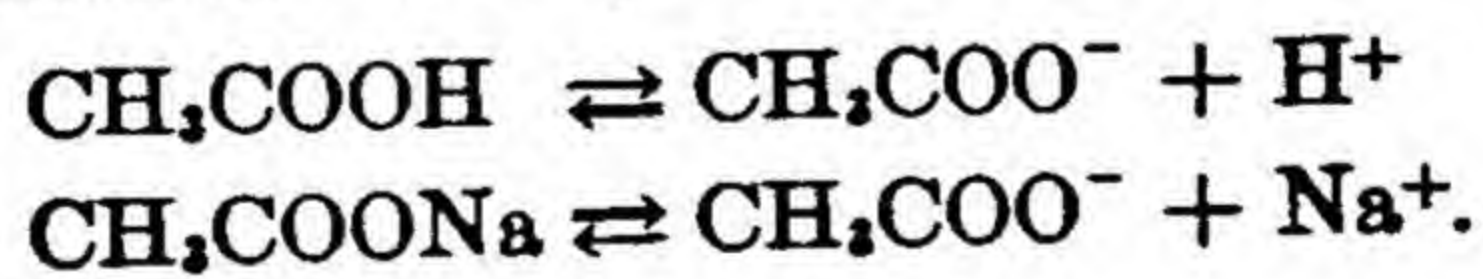


and consistent and constant values of the equilibrium constant,  $K$ , can be calculated from Ostwald's dilution law,  $K = \frac{\alpha^2}{(1 - \alpha)v}$ , where  $\alpha$  represents degree of ionization, and  $v$  is volume.

Pure water at about room temperature is dissociated into its ions to a very slight extent, only sufficiently to give a hydrogen ion activity, ( $H^+$ ), of  $10^{-7}$  molal. The activity of hydroxyl ions, ( $OH^-$ ), is also  $10^{-7}$  molal. Since the activity coefficient may be taken as 1 (unity) at any concentration below 0.001 molal,  $10^{-7}$  is the actual fraction of a gram-ion of both  $H^+$  and  $OH^-$  present in 1000 g. water. In other words, at such low concentrations, the expressions "activity" and concentration have the same meaning. The pH value is 7. (For a definition of pH value see Exp. 37.)

Water of this high degree of purity, however, can be prepared only with great difficulty, and even when prepared it is *subject to easy contamination*, sometimes by solution of small quantities of alkali from glass containing vessels, and also by contamination with  $CO_2$  of the air or  $NH_3$  (from the decomposition of suspended organic matter) or  $HCl$  or other laboratory gases. Frequently in chemical investigations it is desirable to work with solutions having a constant pH value of 7, or of some other unchanging value, and to make this possible so-called "buffer" solutions are often resorted to. (For a good account of buffer solutions, see Rodebush, pp. 214-16; Washburn, *Principles of Physical Chemistry*, pp. 378-80; and Lewis, *A System of Physical Chemistry*, I, pp. 262-4.)

The action of buffers may be explained in the following way. Suppose that we have a mol of acetic acid and a mol of sodium acetate together in an aqueous solution. The ionic equilibria may be represented as follows,



Since sodium acetate is completely ionized, the large concentration of acetate ions, or activity, ( $CH_3COO^-$ ), will repress still further the ionization of the slightly ionized acetic acid, by the "common ion effect," and the activity of hydrogen ions will be relatively small. The pH value of the solution can be adjusted within certain limits by controlling the relative concentrations of the acid and salt. Now, let us pour into this solution a small amount



of acid, say hydrochloric acid. The hydrogen ions thus added will react at once with acetate ions to form non-ionized acetic acid, and since the activity of acetate ions is relatively very high, the hydrogen ion activity will be reduced to practically the original value. The pH value remains almost constant. On the other hand if a small amount of alkali is added, the hydroxyl ions react with hydrogen ions to form non-ionized water and in the meantime the acetic acid dissociates slightly, replenishing the supply of hydrogen ions, and restoring the system to practically the original condition. A solution of this sort is thus able to protect itself against change in pH value, and is said to have "reserve alkalinity and acidity." The solution is also said to be "buffered." Any solution of a weak acid with one of its salts, or of a weak base with one of its salts, acts as a buffer. The degree of buffering and the actual pH value at which the solution is buffered depend not only on the absolute and relative concentrations of the salt and acid (or base), but also on the ionization constant of the acid (or base).

Several useful buffer solution systems have been developed (see Clark, *The Determination of Ions*, 2nd Ed., pp. 99-117). In the present experiment we shall use McIlvaine's system (*J. Biol. Chem.*, 49, 183 (1921)), made by mixing together 0.2 molar  $\text{Na}_2\text{HPO}_4$  solution and 0.1 molar citric acid, and covering a range of pH values from 2.2 to 8.0, in intervals of 0.2. One of the several buffer systems present in human blood is the weak acid  $\text{NaH}_2\text{PO}_4$  and its salt  $\text{Na}_2\text{HPO}_4$ . In this buffer system of McIlvaine, which we are going to use,  $\text{NaH}_2\text{PO}_4$  is undoubtedly formed by reaction of  $\text{Na}_2\text{HPO}_4$  with citric acid. Thus, both  $\text{H}_2\text{PO}_4^-$  (weak acid) and  $\text{NaHPO}_4^-$  (salt of weak acid) are present, as well as citric acid and its salt, sodium citrate.

#### EXPERIMENTAL

(A) Determine the quantity of 0.5 M NaOH solution required to give the indicator color change in a liter of distilled water (conductivity water should be used if available) to which several drops of phenol red indicator have been added. Repeat with 0.5 M HCl solution using methyl red as indicator. Now compare the reserve acidity and alkalinity of water, just determined, with that of a buffered solution having a pH value of 7. Prepare 20 cc. of this solution by adding 16.47 cc. 0.2 M  $\text{Na}_2\text{HPO}_4$  solution



to 3.53 cc. 0.1 *M* citric acid solution. Add phenol red indicator, determine the quantity of 0.5 *M* NaOH solution needed to give the same color change as previously with water, and calculate the quantity required for a *liter* of the buffer solution. Repeat, as before, with 0.5 *M* HCl solution and methyl red indicator.

In making up an indicator color scale for the range of pH values from 2.2 to 8.0, the following indicators (dissolved in water) may be used:

Indicator		pH values between which indicator changes color
Thymol Blue (T.B.)	0.04% solution	1.2-2.8
Brom Phenol Blue (B.P.B.)	0.04% "	3.0-4.6
Methyl Red (M.R.)	0.02% "	4.4-6.0
Brom Thymol Blue (B.T.B.)	0.04% "	6.0-7.6
Phenol Red (P.R.)	0.02% "	6.8-8.4

Table XII sets forth the quantities of stock phosphate and citric acid solutions which should be mixed together to give 10 cc. of the buffer solutions.

Place 10 cc. of the first solution in a test tube labelled pH 2.2, and add 5 drops of the thymol blue indicator solution; then place 10 cc. of the second solution in a test tube labelled pH 2.4 etc., adding 5 drops of the proper indicator to each tube until the whole range from pH 2.2 to 8.0 has been included. Since there is some overlapping in the ranges covered by the different indicators, 40 test tubes are required. These should be arranged in series in a rack. Compare the pH values at which these indicators undergo their characteristic color change as shown by the buffer solutions, with the values found in the hydrogen electrode experiment (Exp. 37). The system of buffer solutions given here has as a matter of fact been standardized by determining the pH values as a function of composition of the solutions by means of the hydrogen electrode.

Once such a color scale has been set up, it furnishes a rapid and convenient method for finding approximately the pH value of unknown solutions. (Of course this method cannot be employed with solutions which are themselves colored.) It is only necessary to take 10 cc. portions of the unknown, and add 5 drops of the various indicators until a color is obtained which matches a color in the scale. In matching colors it is best to remove the



## BUFFER SOLUTIONS

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**TABLE XII**  
**McILVAINE'S BUFFER SOLUTIONS**

pH required	0.2 M $\text{Na}_2\text{HPO}_4$	0.1 M citric acid
	cc.	cc.
2.2	0.20	9.80
2.4	0.62	9.38
2.6	1.09	8.91
2.8	1.59	8.41
3.0	2.06	7.94
3.2	2.47	7.53
3.4	2.85	7.15
3.6	3.22	6.78
3.8	3.55	6.45
4.0	3.86	6.14
4.2	4.14	5.86
4.4	4.41	5.59
4.6	4.68	5.32
4.8	4.93	5.07
5.0	5.15	4.85
5.2	5.36	4.64
5.4	5.58	4.42
5.6	5.80	4.20
5.8	6.05	3.95
6.0	6.32	3.68
6.2	6.61	3.39
6.4	6.93	3.07
6.6	7.28	2.72
6.8	7.73	2.27
7.0	8.24	1.76
7.2	8.70	1.30
7.4	9.09	0.91
7.6	9.37	0.63
7.8	9.58	0.42
8.0	9.73	0.27

desired tube from the rack and to make the comparison with the unknown by looking down the test tubes against a white background. While the scale is in 0.2 pH intervals, it is generally possible to locate intermediate values in an unknown solution to 0.1 pH.

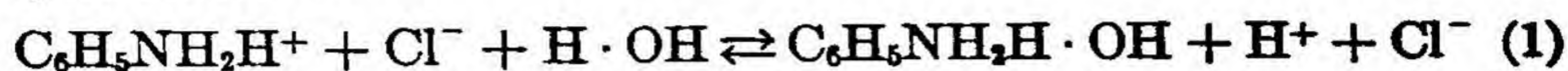
Determine the pH value of four unknown solutions obtained from the instructor.

### (B) DEGREE OF HYDROLYSIS

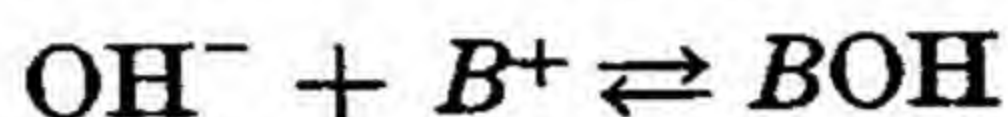
Prepare a fresh solution of 0.1 M aniline hydrochloride, and from it make up 0.01 M and 0.001 M solutions. Determine the pH values of these three solutions by means of the color scale,



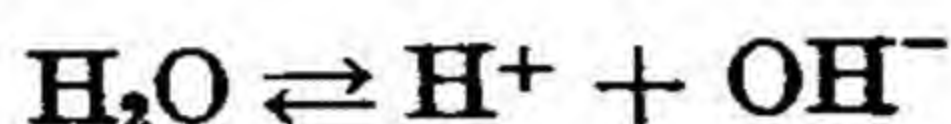
and calculate their hydrogen ion concentrations. In the hydrolytic reaction



the formation of the weak, only slightly ionized base,  $\text{C}_6\text{H}_5\text{NH}_2\text{H} \cdot \text{OH}$ , uses up  $\text{OH}^-$  ions which come from the ionization of water, and this develops an acidity in the solution, due to the liberation of free  $\text{H}^+$  ions. If we let  $B$  represent  $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{H}$  we have two equilibria in this system, namely,



and



Whence, for these weak electrolytes,

$$K_b = \frac{(\text{OH}^-) \cdot (B^+)}{(\text{BOH})} \quad \text{or} \quad \frac{1}{K_b} = \frac{(\text{BOH})}{(\text{OH}^-) \cdot (B^+)} \quad (2)$$

and

$$(\text{H}^+)(\text{OH}^-) = K_{\text{H}_2\text{O}} \quad (3)$$

Now let  $m_0$  be the total molality of the salt  $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}$  present (calculated as if it were entirely in the form of non-ionized molecules), then the degree of hydrolysis  $h$  is given by the following equation

$$hm_0 = (\text{BOH}) = (\text{H}^+) \quad (4)$$

and

$$(1 - h)m_0 = (B^+) \quad (5)$$

Now let us substitute into Equation 2, the value of  $(\text{BOH})$  given by Equation 4, the value of  $(\text{OH}^-)$  given by Equation 3 and of  $(B^+)$  given by Equation 5:

$$\frac{1}{K_b} = \frac{hm_0}{\frac{K_{\text{H}_2\text{O}}}{(\text{H}^+)} \cdot (1 - h)m_0}$$

and then substitute for  $(\text{H}^+)$  the value given by Equation 4, namely  $hm_0$

$$\frac{1}{K_b} = \frac{hm_0}{\frac{K_{\text{H}_2\text{O}}}{hm_0} \cdot (1 - h)m_0}$$

then

$$\frac{K_{\text{H}_2\text{O}}}{K_b} = \frac{h^2m_0}{1 - h} \quad (6)$$



Now, furthermore, from Equation 1, it follows that the hydrolysis constant,  $K_h$ , is given by the equation

$$K_h = \frac{(BOH)(H^+)}{(B^+)}$$

since  $(H \cdot OH)$  may be taken as 1, and  $(Cl^-)$  may be taken as the same before and after the hydrolytic reaction. Therefore, from Equations 4 and 5

$$K_h = \frac{m_0 \cdot hm_0}{(1-h)m_0} = \frac{h^2m_0}{1-h}$$

Consequently from Equation 6, it follows that

$$K_h = \frac{K_{H_2O}}{K_b} = \frac{h^2m_0}{1-h}$$

In a similar manner an equation for the hydrolysis of the salt of a weak acid and strong base may be derived,

$$\frac{K_{H_2O}}{K_a} = \frac{h^2m_0}{1-h}$$

(See Rodebush, pp. 207-210.)

Calculate the degree of hydrolysis for 0.1, 0.01 and 0.001 *M* aniline hydrochloride solutions and, using Equation 6, calculate  $K_b$  for aniline. Compare the values for degree of hydrolysis and for  $K_b$  with those found in a table of constants.

### (C) IONIZATION AND CHEMICAL CONSTITUTION

Using the color scale, as already described, and the indicators thymol blue and brom phenol blue, determine the pH values of the following stock solutions. (3) and (4) may lie slightly beyond the range of the color scale, but their pH values can be roughly estimated.

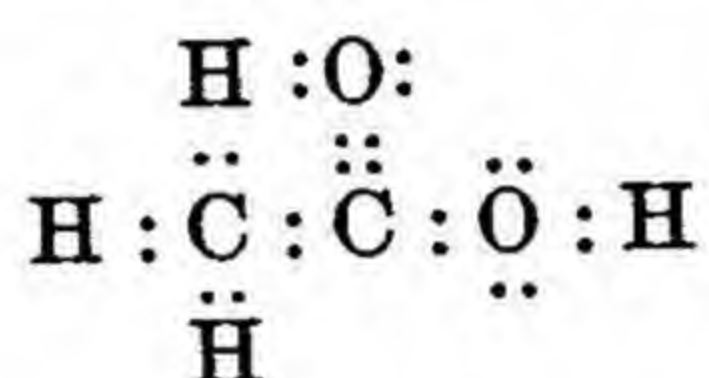
- (1) 0.01 *M* acetic acid
- (2) 0.01 *M* chlor-acetic acid
- (3) 0.01 *M* dichlor-acetic acid
- (4) 0.01 *M* trichlor-acetic acid
- (5) 0.01 *M* brom-acetic acid
- (6) 0.01 *M* propionic acid
- (7) 0.01 *M*  $\alpha$ -brom-propionic acid



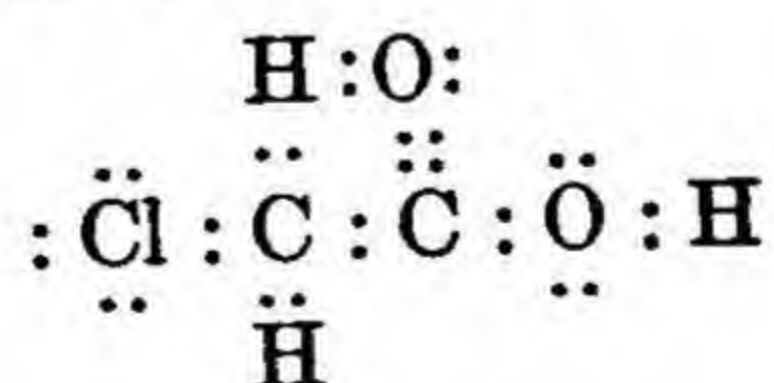
- (8) 0.01 *M*  $\beta$ -brom-propionic acid
- (9) 0.01 *M* benzoic acid
- (10) 0.01 *M* *o*-nitro-benzoic acid
- (11) 0.01 *M* *m*-nitro-benzoic acid

From the observed pH values calculate the hydrogen ion concentration for each acid, and from this the degree of ionization, and finally the ionization constant. Compare the values so obtained for ionization constants with those found in tables, remembering, however, that for the strong acids involved, the ionization constant varies with concentration, and also remembering that the color scale method yields the correct order of magnitude only, and not the precise numerical value. (See also Exps. 14 and 30.)

In explanation of the degree of ionization as a function of chemical constitution one theory which has been advanced may be briefly mentioned. The formula for acetic acid may be written



where the dots represent electrons. Nothing whatever is implied in this diagrammatic representation regarding the structure of the atom; the dots merely represent the number of valence electrons in the outer shells of the atoms. When acetic acid is dissolved in water, the pair of electrons which binds the hydrogen atom to the oxygen is on the average probably drawn over slightly toward the oxygen and away from the hydrogen, thus occasionally giving the positively charged hydrogen a chance to break away as an ion, probably to form the ion  $\text{OH}_3^+$  by combination with  $\text{H}_2\text{O}$ . About 1 per cent of the acetic acid molecules are ionized in a 10 per cent solution. If now one of the hydrogen atoms of the methyl group is replaced by chlorine



the strong attraction of the chlorine atom for electrons displaces the electrons of the methyl carbon toward the left, and this dis-



placement in turn causes a shift toward the left of the electrons on the next carbon atom, and finally on the oxygen atom, thus moving the pair of electrons further away from the hydrogen atom and permitting it to ionize to a greater extent. With dichlor- and trichlor-acetic acids the effect is even more pronounced. The effect is not so large with bromine and iodine, possibly because their atomic volumes are larger and hence the attraction of the positive nucleus for electrons in the outer shell is less than with chlorine. The various degrees of ionization observed in the above experiment may be accounted for in terms of this theory.

Dr. Langmuir (in *Chemical Reviews*, 6, 465-67 (1929)) has given a particularly interesting Boltzmann factor treatment of the ionization of such acids as those that the student has just studied, and it will be well worth the student's time to develop his own results in the same way. To do this, construct a table, listing the acids in the first column, and in the second column, under the heading  $K$ , list the respective ionization constants which have just been calculated, above. In the third column, under the heading  $\ln \frac{K}{K_{ac}}$ , list the natural logarithms of the ratio of  $K$  for every acid to  $K_{ac}$  for *acetic acid*. It can be shown by a Boltzmann factor treatment that this term,  $\ln \frac{K}{K_{ac}}$ , should be equal to  $\frac{\lambda}{kT}$  where  $\lambda$  is the difference between the work necessary to remove a hydrogen ion from the given acid molecule and from an acetic acid molecule;  $k$  is the Boltzmann gas constant ( $R \div 6.06 \times 10^{23}$ ) and  $T$  is the absolute temperature.

This can be shown as follows. For a weak acid the degree of ionization is so small that the Ostwald dilution law equation

$$\frac{\alpha^2}{(1-\alpha)_v} = K \text{ reduces to the form } \frac{\alpha^2}{1} = K \cdot v, \text{ or } \frac{\alpha}{1} = \sqrt{K \cdot v},$$

where  $\frac{\alpha}{1}$  represents the ratio of the number of H atoms in the form of ions per unit volume to the number of H atoms remaining in the non-ionized acid molecules per unit volume. If we let  $W$  represent the work which is done in separating a mol of acid into its ions  $H^+$  and  $A^-$ , we may consider that  $1/2 W$  is the work required to separate the mol of  $H^+$ . Then from the Boltzmann law it follows that the relative probabilities and relative numbers of H atoms in



the ionized and non-ionized states, per unit volume, are

$$\frac{P_{H^+}}{P_{HA}} = \frac{n_{H^+}}{n_{HA}} = e^{-\frac{W/2}{RT}}$$

since the hydrogen ions are being lifted out of an acetic acid molecule by the expenditure of energy in very much the same way as air molecules were lifted from a low to a higher level in the atmosphere in the treatment of Exercise III. Hence, also

$$\frac{n_{H^+}}{n_{HA}} = \frac{\alpha}{1}, \text{ and therefore, } e^{-\frac{W/2}{RT}} = \sqrt{K \cdot v}.$$

Squaring both sides, we get

$$e^{-\frac{W}{RT}} = K \cdot v \quad (7)$$

and writing the same equation for acetic acid, we get

$$e^{-\frac{W_{ac}}{RT}} = K_{ac} \cdot v. \quad (8)$$

Now, let us divide Equation 7 by Equation 8:

$$e^{+\frac{W_{ac} - W}{RT}} = \frac{K}{K_{ac}}.$$

Finally, if we let  $\lambda$  represent the difference in work in the case of the two acids per single molecule, we have

$$\lambda = (W_{ac} - W) \div 6.06 \times 10^{23}, \text{ and } \frac{\lambda}{kT} = \ln \frac{K}{K_{ac}}.$$

Construct a fourth column in the above table, headed  $\lambda$ . This  $\lambda$ , as we have just indicated, is the difference between two small quantities of energy; in this column  $\lambda$  is to be expressed in a unit of electrical energy, namely in volt-electrons, or what is the same thing, in volt-protons, or in volts  $\times$  the charge on  $H^+$ , only instead of using electrostatic or electromagnetic units of charge, let us call the charge on an electron, or on one  $H^+$ , unity. (See Exercise I.) Then since  $R = 8.315$  volt-coulombs,

$$kT = \frac{8.315 \times 298 \text{ (room temp.)}}{6.06 \times 10^{23}} = 4.08 \times 10^{-21} \text{ volt-coulombs.}$$

But in one coulomb there are  $\frac{6.06 \times 10^{23}}{96,500} = 6.28 \times 10^{18}$  elec-



trons. Therefore  $kT = 4.08 \times 10^{-11} \times 6.28 \times 10^{18} = 25 \times 10^{-6} = 0.025$  volt  $-H^+$  charge. Multiply the  $\ln \frac{K}{K_{ac}}$  values of the third column in the table by 0.025 to get the respective values of  $\lambda$  in this unit, volt  $-H^+$  charge. Compare the values of  $\lambda$  obtained in the case of the different acids, since  $\lambda$  gives a measure of the influence of the substituent atom, Cl, Br, etc., and of the position of the substituent atom in the molecule, on the ionizability of the  $H^+$ ; in other words, the larger  $\lambda$  is, the more readily the acid forms  $H^+$ .

**REFERENCES:**

- Taylor, Chap. XII.
- Rodebush, Chap. IX.
- Getman and Daniels, Chaps. XVI and XVII.
- Millard, Chap. VIII.
- Findlay, Chap. XV.
- Clark, *The Determination of Hydrogen Ions*.
- Newman, *Electrolytic Conduction*.
- Glasstone, *Electrochemistry of Solutions*.



## EXPERIMENT 39

### UNIT CELL SIZE OF SODIUM CHLORIDE LATTICE; GROWTH RATIOS AND HABIT MODIFICATIONS OF CRYSTALS

In a laboratory course of the sort for which this manual is written it will naturally be impossible to introduce the student to the technique of X-ray analysis of crystals, because of the expensive equipment and the time required to carry such analyses

through to a conclusion. In the present experiment the student may profitably get a taste of some of the simple principles of crystal structure.

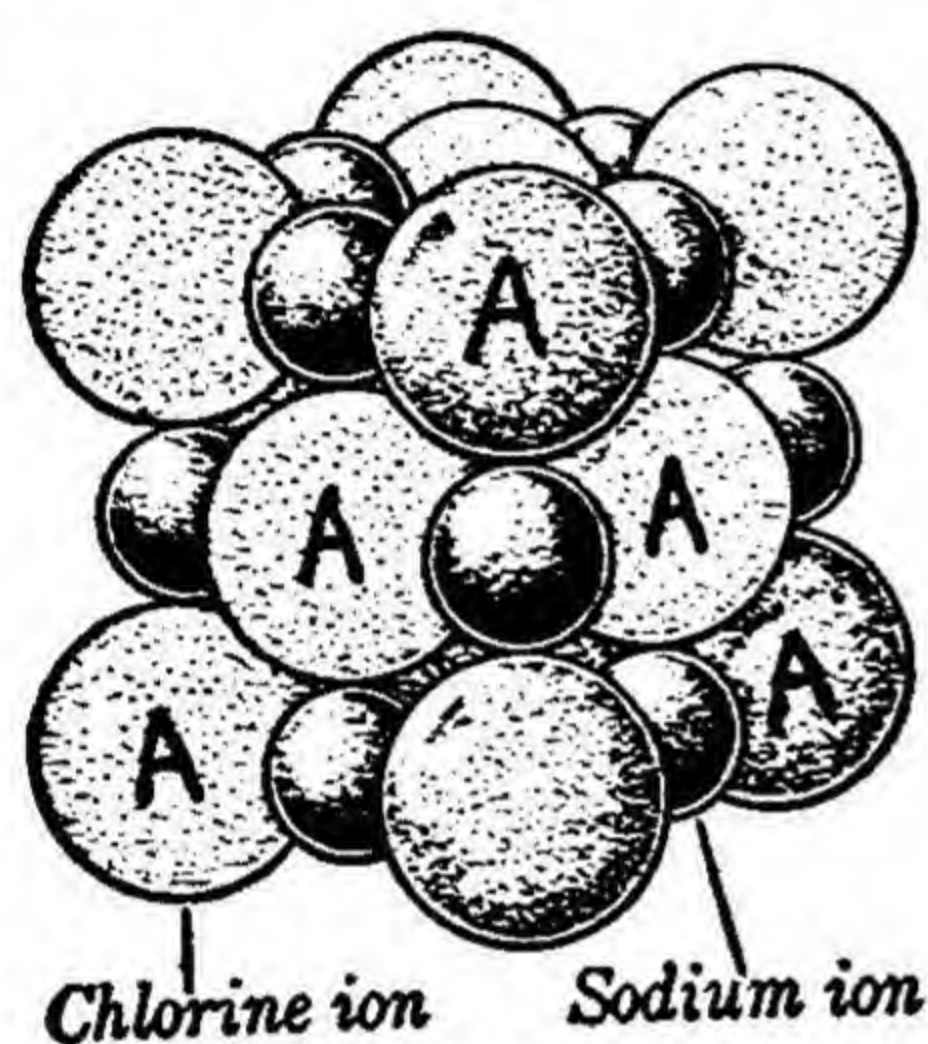


FIG. 65

X-ray analysis shows that in the regular three-dimensional array of particles, which make up what we call the crystal *lattice* of NaCl, the sodium ions,  $\text{Na}^+$ , and chlorine ions,  $\text{Cl}^-$ , are arranged as shown in Fig. 65. The dark balls represent  $\text{Na}^+$  ions and the light balls  $\text{Cl}^-$  ions. In such a lattice, it is

always possible to pick out a *unit cell*, that is, the simplest unit or structure considered from a geometrical point of view which, when repeated over and over again in all directions, will give the whole lattice. The unit cell in the case of NaCl may be chosen as that tiny cube which has its 8 corners at the centers of the eight chlorine ions which are located at the 8 corners of the cubical cluster in Fig. 65. If such a unit cell is cut out of the lattice of Fig. 65, a face of the unit cell would appear as in Fig. 66. The chlorine ions at the centers of faces have been cut into halves, those at the corners into eighths, and the sodium ions along the edges into fourths, as is to be expected, of course, since two cubes can be placed together face to face, eight cubes contracting at a corner, and four along an

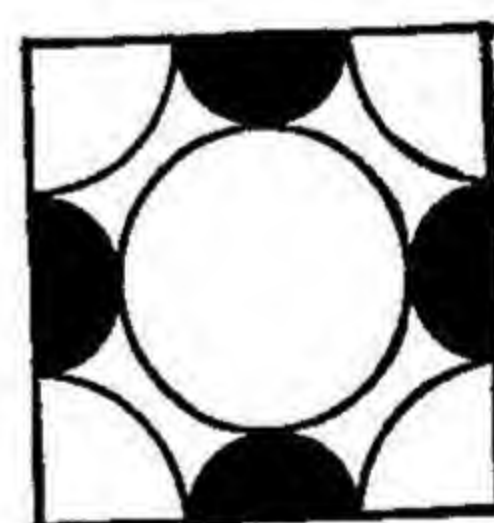


FIG. 66



## UNIT CELL SIZE OF SODIUM CHLORIDE LATTICE 275

edge. Counting up all the pieces of ions belonging to the unit cell cube, we find altogether 4  $\text{Na}^+$  and 4  $\text{Cl}^-$ ; namely, for the  $\text{Na}^+$ ,  $12 \times 1/4$  along the 12 edges plus the 1 whole  $\text{Na}^+$  at the center of the cube (not visible in the figures); and for the  $\text{Cl}^-$ ,  $8 \times 1/8$  at the 8 corners plus  $6 \times 1/2$  at the 6 faces.

**Unit Cell Size.** Since density is an intensive rather than an extensive property, i.e., it does not depend on the *quantity* of the substance, the density of the unit cell is the same as the density of a large piece of NaCl. Select two crystals of rock salt weighing about 1 to 2 grams, or more, and weigh each one accurately in air (making buoyancy correction) and in benzene, hanging the crystals from a fine wire. With a pycnometer determine the density of benzene at room temperature (see Exp. 9) and then calculate the volume displaced by each crystal. From this volume and the weight of the crystal calculate the density of each, and average the two results. From the mass of unit cell ( $4\text{Na}^+$ ,  $4\text{Cl}^-$ ) and the density calculate the volume, and edge length,  $L$ , of the unit cell.

$$L = \sqrt[3]{\frac{4 \times \text{mol. wt. NaCl}}{6.06 \times 10^{23} \times \text{density}}}$$

$L/2$  is the distance between the horizontal or vertical layers of ions, and is also the closest distance between  $\text{Na}^+$  and  $\text{Cl}^-$ . How does your result compare with the accepted value? What are the accepted values for the ionic radii of  $\text{Na}^+$  and  $\text{Cl}^-$ ?

Unless special care is taken crystals seldom grow perfectly. They usually undergo some distortion due to their environment or to the presence of foreign materials capable of being adsorbed by the growing crystal. Changes in form resulting in the development or repression of the crystal faces are known as habit modifications. Two examples of habit modification will be considered in the following experiments—one, the formation of octahedra when sodium chloride is grown in the presence of urea, and the other the enlargement of the cube faces and reduction of the octahedral faces of potassium alum when grown in the presence of certain dyes. These habit modifications are brought about by the selective adsorption of the foreign materials by certain crystal faces. In Fig. 65 the horizontal and vertical planes of ions parallel to the cube faces are known as 100 planes (pronounced “one-zero-



zero"), and the planes such as A-A-A-A-A in Fig. 65, running from a cube corner to the diagonal of a cube face, are known as 111 planes (pronounced "one-one-one").

In the case of the potassium alum only the cube (100) faces are colored by the dye, Fig. 67, A and B. The change in habit is also accompanied by a change in the growth ratio of the crystal. By

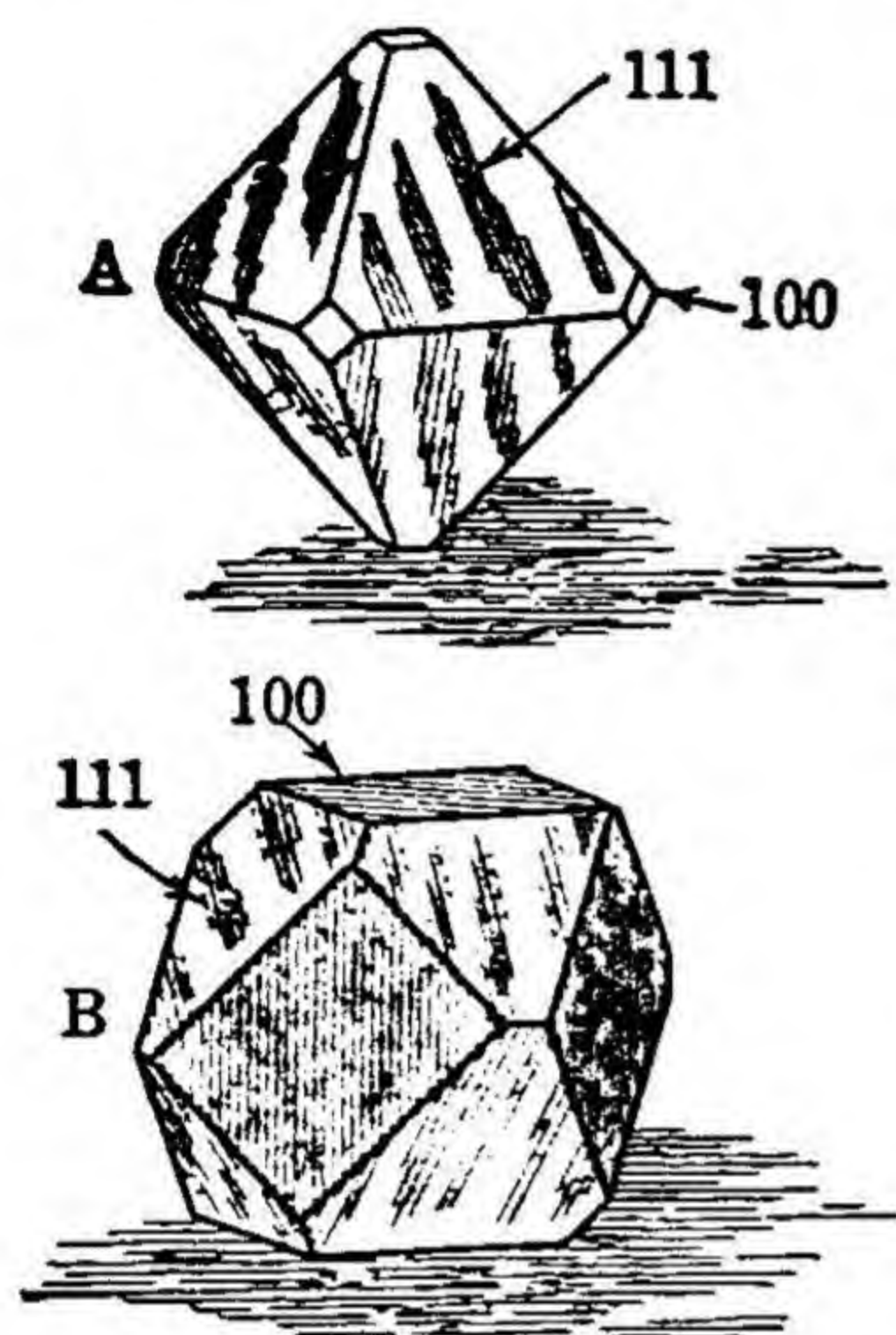


FIG. 67

the growth ratio is meant the ratio of the perpendicular distance between a pair of parallel faces of one kind to the perpendicular distance between a pair of parallel faces of another kind. Thus in the case of potassium alum the growth ratio is obtained by dividing the distance between one pair of cube faces (100) by the distance between one pair of octahedral faces (111). It is designated as follows:  $V_{100}/V_{111}$ . The growth ratio is a characteristic and constant value for any normally and freely growing crystal. Any change in its value means that the rate of growth (perpendicular displacement) of one kind of face has

been altered to a greater extent than that of another kind. Since the adsorption of foreign materials by crystal faces results in a repression of the face displacement it is evident therefore that the measurement of the growth ratio affords a means of determining whether a given substance is selectively adsorbed by a crystal.

#### THE MODIFICATION OF THE CRYSTAL HABIT OF SODIUM CHLORIDE BY UREA

Prepare two sodium chloride solutions saturated at about 50° C. To one of these add enough urea to make its concentration in the salt solution about 15%. Let these solutions cool slowly to room temperature and permit the crystals to grow by slow evaporation at room temperature for several days. Examine the crystals with a magnifying glass or microscope and note that those grown in the presence of the urea are octahedral and the others are cubical.



## UNIT CELL SIZE OF SODIUM CHLORIDE LATTICE 277

### THE GROWTH RATIO AND THE HABIT MODIFICATION OF POTASSIUM ALUM BY ADSORBED DYES

Place a solution of potassium alum saturated at about 80°–90° C. in a crystallizing dish and cool slowly to room temperature. Allow the crystals to grow by slow evaporation until some well formed crystals have been grown. Select six of these having dimensions of about 3–5 mm. Each of these is fastened to the end of a short length of nichrome wire by gently heating the wire and pushing it into one of the octahedral faces. The other end of the wire is securely fastened to a deeply notched cork stopper fitting a shell vial approximately 62 × 20 mm. A solution of potassium alum saturated at 25° is placed in three shell vials and a like solution, to which has been added 0.05 g./100 cc. of Diamine Sky Blue FF (or Pontamine Blue or Bismarck Brown) dye, is placed in three other shell vials. The corks are then numbered for reference and the distances between the three pairs of parallel octahedral faces (not including the pair through which the wire was inserted) of each crystal is measured by means of calipers and a millimeter scale. The distances between the three corresponding pairs of parallel cube faces are also measured. The measurements are recorded and the corks with their attached crystals are then loosely fitted in the shell vials containing the potassium alum solutions. The shell vials are then placed in a large beaker in a thermostat adjusted to 25° C. The crystals are permitted to grow by slow evaporation and the measurements repeated in about 24 hours. Be careful to record the measurements of each crystal correctly. At the end of another 24 hour period the measurements are again made. The perpendicular distances between the cube faces are then plotted as ordinates against the corresponding perpendicular distances between the octahedral faces as abscissas. From the straight line connecting the points the growth ratio  $V_{100}/V_{111}$  is determined for each of the crystals grown in the presence and absence of the dye. Note the change in the growth ratio and the habit modification produced by the dye.

The crystal lattice of potassium alum is such that the cube planes are populated by ions of like charge and the octahedral planes are populated by a checkerboard arrangement of ions of



unlike charge. The crystal lattice of sodium chloride, Fig. 65, shows that the cube planes of NaCl are populated by unlike ions whereas the octahedral planes are made up of like ions.

Considering that in the planes made up of ions of unlike charge there is a partial polarization of the positive and negative fields of the ions with a consequent reduction in the attractive force of the plane as a whole, whereas in those planes made up of ions of like charge there is no such effect, account for the differences in the habit modifications observed in the above experiments.

#### REFERENCES:

- Taylor, Chap. V.
- Rodebush, Chap. IV.
- Getman and Daniels, Chap. IV.
- Millard, Chap. IV.
- Findlay, Chap. VI.
- Bunn, *Proc. Roy. Soc.*, **A141**, 567 (1933).
- Buckley, *Z. Krist.*, **81**, 157 (1932).
- Colloid Symposium Annual*, VII, 59 (1930).
- Alexander, *Colloid Chemistry*, vol. I, p. 586.
- Bancroft, *Applied Colloid Chemistry*, pp. 199-205, McGraw-Hill.



## EXPERIMENT 40

### THE ADSORPTION OF OXALIC ACID BY CARBON

It has long been known that many dissolved substances may be removed from their solutions upon being shaken up with a finely divided solid such as charcoal. What happens is that the dissolved substance collects in the boundary formed by the contact of the solid with the solution. The concentration in this boundary layer is therefore different from that in the solution. Such a change in concentration at an interface is termed an *adsorption*. Since the concentration in the boundary layer may in some instances be decreased rather than increased this fact is recognized by referring to an increase as a positive adsorption and a decrease as a negative adsorption. In addition to the solid-liquid boundary, adsorption occurs at solid-gas, liquid-gas and liquid-liquid interfaces.

It is evident that adsorption is a boundary phenomenon and as such not only involves concentration changes but is also related to accompanying changes in surface energy. Willard Gibbs (*Trans. Conn. Acad.*, 3, 439 (1876)) recognized this and first established the mathematical relationship between surface tension and surface concentration in the following equation:

$$u = - \frac{c}{RT} \frac{d\gamma}{dc} \quad (1)$$

where  $u$  is the excess solute per sq. cm. in the boundary layer,  $\gamma$  is the surface tension,  $c$  the concentration of the solution, and  $R$  and  $T$  are the gas constant and absolute temperature. This equation shows that an adsorption ( $u$ ) is positive when the surface tension of a solution decreases with an increase in solute concentration and conversely an adsorption ( $u$ ) is negative when the surface tension of a solution increases with an increase in concentration.

The experimental verification of the Gibbs' adsorption equation presents a number of difficulties depending upon the type of



interface concerned. Thus while at a gas-liquid or liquid-liquid interface the surface or interfacial tension can be measured it is difficult to determine the concentration in the actual boundary layer. On the other hand in the case of a solid-liquid or solid-gas interface the concentration in the boundary layer can be determined but any measurement of the interfacial tension is extremely difficult.

A more frequently used expression is a modified form of the Freundlich equation

$$\Delta\gamma = sc^{\frac{1}{n}} \quad (2)$$

already referred to in Experiment 11. The symbols  $s$  and  $n$  represent constants. This relates the lowering of the surface tension to the concentration in moderately concentrated solutions. Since the quantity of substance adsorbed and the change in surface tension are closely related the above equation may be written as follows

$$\frac{x}{\sum\omega} = k \cdot c^n \quad (3)$$

in which  $\sum\omega$  is the total interfacial area,  $x$  is the quantity adsorbed,  $c$  is the equilibrium concentration (i.e., the concentration after the adsorption has occurred) of the solution and  $k$  and  $n$  are constants.

The total interfacial area  $\sum\omega$  of most solids is quite difficult if not impossible to determine. However if the solid is finely divided and of uniform structure and particle size one can assume without great error that equal masses have equal surfaces and substitute the mass  $m$  for  $\sum\omega$  in the above equation. In this case the constants  $k$  and  $n$  are constant only for the one particular lot of the solid for which they have been determined.

This equation

$$\frac{x}{m} = k \cdot c^{\frac{1}{n}} \quad (4)$$

is known as the equation of the adsorption isotherm and will be used in the following experiment on the adsorption of oxalic acid by activated carbon.



## ADSORPTION OF OXALIC ACID BY CARBON 281

### EXPERIMENTAL

Place 200 cc. of each of the following oxalic acid solutions in 500 cc. Erlenmeyer flasks:  $N/5$ ,  $N/10$ ,  $N/20$ ,  $N/30$ ,  $N/40$ ,  $N/50$ ,  $N/100$  and  $N/200$ . To each flask add 1 g. of activated carbon. Blood or animal charcoal, sugar charcoal, Norit, or Suchar or Nuchar will serve, but it is much more satisfactory to use activated coconut charcoal of large enough grain size so that it can easily be shaken free of fine dust on a sieve. Size 8–10 mesh (i.e., through 8 mesh and caught on 10 mesh screens) is very satisfactory, although smaller sizes may be used.\*

Shake each flask vigorously at about 10 minute intervals for one or two hours and then let stand for several hours to permit complete settling of the charcoal. Pipette out 50 cc. portions of solution from each flask, being careful not to remove any of the carbon. If this cannot be done the solutions must be filtered through as small a filter as possible before removing the 50 cc. portions. Why? These 50 cc. portions are then titrated with a  $N/5$   $\text{KMnO}_4$  solution. From the values thus obtained calculate the amount of oxalic acid remaining in the solution and that adsorbed by the carbon at each concentration. Plot the values for the equilibrium concentration using the number of cc. of  $\text{KMnO}_4$  required for the oxidation as abscissas and the actual amounts of oxalic acid ad-

\* Ordinary wood charcoal is not a very active adsorbent. It must first be "activated." Good activated charcoal can be made from coconut shells (or from peachstones, cherry pits, nutshells, or any form of dense wood, or even from ordinary wood charcoal) by first breaking up the carbonaceous material into small pieces, about 1 cm. to an edge, and then heating at  $350^\circ$ – $400^\circ$  C., in a covered tin can (with holes punched in the lid) until volatile matter stops coming off. (It is a good idea to ignite the disagreeable acrid gases with a match so that they will burn.) When the charcoal is cool, crush it and sieve off about 200 g. of 6–8 mesh grains. Place this in the middle of a quartz combustion tube, or iron pipe, and while heating it in an electric furnace at about  $900^\circ$  C. (thermocouple) pass steam from a flask of boiling water through it for about 2 hours at a rate of about 1 g. water per minute.

This yields an excellent carbon. Not much is known about the details of the mechanism of activation. The water vapor at this temperature ( $900^\circ$ ) undoubtedly acts as a mild oxidizing agent and chews into the carbonaceous mass, increasing the porosity and at the same time probably cleaning out resinous and tarry materials adhering to the internal sponge-like structure of the carbon, or at any rate making the porous network of carbon atoms more powerfully adsorbent.



orbed by the carbon as ordinates. Take logarithms of both sides of Equation 4, and plot  $\log \frac{x}{m}$  against  $\log c$  (abscissa). The former curve should be parabolic and the latter linear. What reasons can be given to account for any deviation from these characteristic forms of the curves? In the latter plot what is the meaning of the slope; of the intercept? Why does the first curve go through the origin, but not the second one?

**References:**

- Taylor, Chaps. VI and XV.
- Rodebush, Chaps. VIII and XIV.
- Getman and Daniels, Chap. X.
- Millard, Chaps. IV and XVI.
- Findlay, Chaps. IV and XX.
- Bancroft, *Applied Colloid Chemistry*, Chap. I.
- Kruyt and van Klooster, *Colloids*, p. 26.



## EXPERIMENT 41

### RATE OF SETTLING OF FINE PRECIPITATES; DISTRIBUTION OF GRAIN SIZE

Pigments, soils, and fine powders seldom if ever contain particles of uniform diameter. Since such properties as "covering power" and tensile strength of paint films, water holding capacity of soils, extent of surface reactions, and sensitivity of photographic emulsions, are related to particle size, it frequently becomes desirable to know the per cent distribution of the various sized particles present, in selecting a given material for some specific use. While many methods have been devised to determine size distribution, one of the simplest and most convenient is that of W. J. Kelly described in *J. Ind. Eng. Chem.*, 16, 928-30 (1924) and also in the *Colloid Symposium Monograph*, Vol. 2, pp. 29-36 (1925). This is a modification of Ostwald and Von Hahn's method and makes use of the fact that a suspension of a powder is specifically heavier than the pure suspension medium. Therefore, when a suspension is placed in one arm of a U-tube and the pure medium in the other arm, the former will stand at a lower level than the latter. As the suspended solid settles out the density of

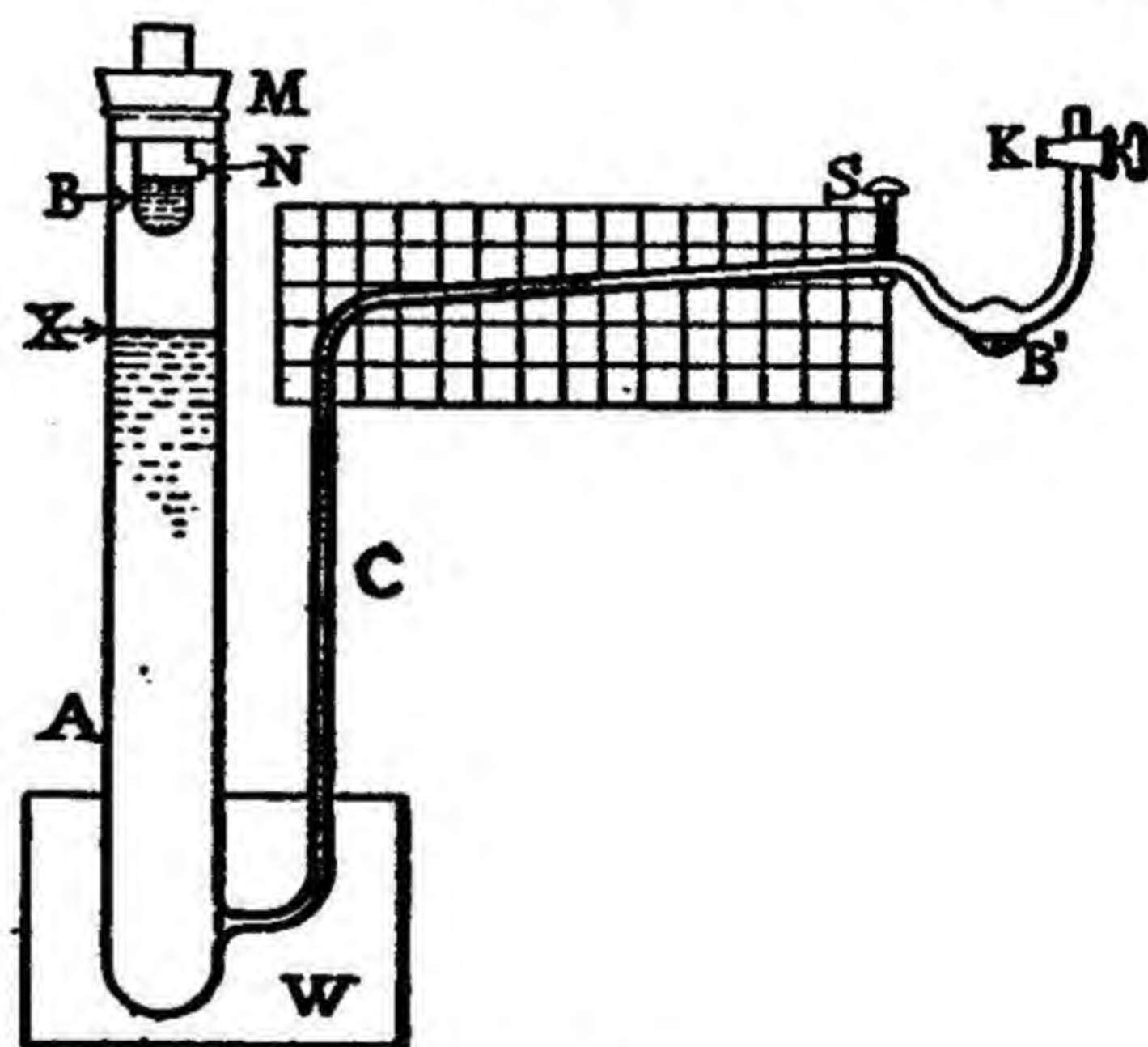


FIG. 68

the suspension becomes less and the levels in the tubes approach the same value. By observing the rate at which the level difference changes, the rate of settling can be determined. Instead of a U-tube the Kelly apparatus is of the form indicated in Fig. 68. The tube A contains the suspension and the capillary side arm C the



pure medium. By bending the capillary arm as shown the apparent difference in the levels is increased and can be measured by the length of the liquid column in the almost horizontal section. This difference in level,  $a$ , is given by the following equation

$$a = \frac{D}{d} h - h \quad (1)$$

in which  $D$  is the density of the suspension,  $d$  that of the medium and  $h$  the height of the suspension. If  $l$  is the length of the column in the almost horizontal section of the side tube and  $b$  the small angle made by this section with the true horizontal,  $a$  can be expressed as follows

$$a = l \sin b. \quad (2)$$

The weight of material settling past the side tube is obtained as follows (quoted directly from the original article): "... the density of the suspension,  $D$ , has to be known in terms of the medium and the specific gravity of the suspended material. Thus

$$D = \frac{Vd - vd + w}{V} \quad (3)$$

where  $V$  is the volume of suspension in the large tube above the side tube,  $v$  the volume of the pigment and hence also that of the medium displaced, and  $w$  is the weight of the solid phase.

"If  $S$  is the specific gravity of the pigment, then

$$S = \frac{w}{v} \quad \text{or} \quad v = \frac{w}{S}. \quad (4)$$

Substituting (4) in (3)

$$D = \frac{Vd - \frac{wd}{S} + w}{V} = \frac{SVd - wd + wS}{VS}. \quad (5)$$

Substituting (5) and (2) in (1)

$$l \sin b = \frac{h}{d} \frac{SVd - wd + wS}{VS} - h$$

which on simplification gives

$$w = \frac{SV dl \sin b}{h(S - d)}. \quad (6)$$



In this equation  $w$  and  $l$  are the only variables for any given experiment, and as soon as the values of the constants have been determined the equation may be written

$$w = K \cdot l \quad (7)$$

in which form it is easily used. The total weight of solid phase in the suspension being known, it is a simple matter to calculate the percentage which settles out in a given time.

"In using this method the actual length of the side tube is immaterial, provided it is long enough to take care of the recession due to the settling. The zero point is taken at the upper end of the tube and the difference between this point and the position of the meniscus at any given time is taken as  $l$ . In this way the effect of capillarity is eliminated."

#### PROCEDURE

It is important in size distribution determinations that the particles exist as individuals when suspended in the suspension medium. The sample must therefore be prepared in such a way that all aggregates of particles are broken up. This is accomplished by moistening a weighed amount of the powder with a few cubic centimeters of a 5% gum arabic sol to which has been added a small quantity of electrolyte (for a 2% barium sulfate suspension about 1 cc. of a 5% barium chloride solution is satisfactory). This mixture is rubbed well on a glass plate with a spatula, washed into a glass graduate and diluted to the required volume.

Having prepared 100 cc. of a 2% aqueous barium sulfate suspension as directed above, next clean thoroughly the sedimentation tube and capillary with hot dichromate-sulfuric acid solution, and rinse with distilled water. Replace the tube in its supporting frame and adjust the screw S so that the angle  $b$  is about one and one-half degrees. The fragile junction of the capillary to tube A should be supported by mounting on a block of wood W, or something that will serve the same purpose. Open the stop-cock K and fill the apparatus with distilled water to such a height that the meniscus in the capillary side tube rests at the lower end of the horizontal section. The corresponding level is marked X on the large tube and its height  $h$  above the side tube measured. The water is then drawn up to the end of the capillary tube, the stop-



cock closed, and the large tube emptied. The suspension is then poured into the large tube up to the mark X and thoroughly stirred. After inserting the stopper M carrying the bulb B, filled with water up to the holes N, the stop-cock is opened and the position of the meniscus in the capillary tube determined at various time intervals. The water in the bulbs B and B' ensures a constant aqueous vapor pressure below the stopper and above the capillary meniscus, thus preventing the introduction of errors due to evaporation.

Since the initial rate of settling is uniform the zero or starting point of the meniscus may be determined by plotting the first few readings as ordinates against time as abscissas and extending the line so obtained back to cut the ordinate at zero time. This value is then taken as the zero value for the experiment. Readings should be taken every minute for about ten minutes, followed by a gradual lengthening of this interval as the rate of settling decreases, and should be continued over a period of about 6 hours.

From the readings thus obtained the values of  $w$  and the per cent settling in the various time intervals are calculated. A sedimentation curve is then constructed by plotting the per cent settled as ordinates against time as abscissas. With the Latshaw tangentimeter described in Exp. 8, draw a number of tangents to the curve corresponding to different time intervals. The difference between the intercepts of any two tangents on the weight axis corresponds to the amount of material having a size range which can be calculated for that time interval from Stokes' law.

In using Stokes' law

$$r^2 = \frac{9}{2} \frac{\eta \cdot h}{(S - d)g \cdot t},$$

$S$ ,  $d$ , and  $h$  have the same values as in Equation 6,  $\eta$  is the coefficient of viscosity of the medium,  $t$  the time in seconds, and  $r$  the radius of the particles. At any given time interval the particles having a radius calculated from Stokes' law for this time interval will have settled past the opening of the side tube. Therefore the range of particle size settling between successive time intervals can be obtained by calculating the radii corresponding to such time intervals. From these values the size distribution curve is constructed by plotting the per cent of each class size as ordinates against the size in microns as abscissas.



The value of the sine of angle  $b$  for the apparatus is readily determined by placing a strip of coördinate paper back of the horizontal part of the capillary tube and reading the tangent of the angle directly, from which the sine is calculated. A portion of a small graduated pipette may be used for the long, almost horizontal section of the capillary tube, thus providing a scale whose values are readily calibrated in units of length.

Table XIII contains the data obtained in a typical determination. Table XIV contains the data for the construction of the size-distribution curve.

TABLE XIII

Time	Minutes	Reading	$l$ (cm.)	Weight settled (g.)	Per cent settled
1:30		(0.266)			
1:31	1	.269	0.071	0.0107	0.54
1:32	2	.272	.142	.0214	1.07
1:33	3	.275	.214	.0323	1.62
1:34	4	.279	.309	.0467	2.34
1:35	5	.283	.404	.0610	3.05
1:37	7	.294	.666	.1006	5.03
1:40	10	.303	.881	.1330	6.65
1:45	15	.320	1.285	.1940	9.70
1:50	20	.341	1.785	.2695	13.50
1:57	27	.383	2.78	.420	21.0
2:10	40	.423	3.74	.564	28.2
2:25	55	.453	4.45	.672	33.6
2:45	75	.480	5.09	.769	38.5
3:20	110	.502	5.62	.849	42.5
3:45	135	.520	6.04	.912	45.6
4:30	180	.538	6.47	.977	48.9
5:15	225	.550	6.75	1.011	50.6
6:50	320	.561	7.02	1.060	53.0
7:30	360	.564	7.09	1.071	53.6

Sine of angle of inclination = 0.030

Volume above side-arm = 99 cc.

Temperature = 24°

$h$  = 25.2 cm.

\*0.1 cc. = 2.38 cm.

Zero reading = 0.266

Density of  $\text{BaSO}_4$  = 4.5

Density of  $\text{H}_2\text{O}$  = 0.997

$$w = \frac{d \cdot V \cdot S \cdot l \sin b}{h(S - d)} = \frac{0.997 \times 99 \times 4.5 \times l \times 0.03}{25.2(4.5 - 0.997)} = 0.151 l$$

\* Calibration of scale reading on horizontal section of capillary tube which in this instance was a small volume pipette.



TABLE XIV  
DISTRIBUTION OF PARTICLE SIZE IN BaSO<sub>4</sub> SUSPENSION

$$\begin{aligned} r^2 &= \frac{9}{2} \frac{\eta h}{(S - d) g \cdot t} \\ &= \frac{9}{2} \times \frac{0.0092 \times 25.2}{(4.5 - 0.997) \times 980} \times \frac{1}{t} \\ &= 0.000304/t \end{aligned}$$

Time	Radius (microns)	Per cent
1200 sec.	—5.0	2.0
2400	5.0—3.5	5.5
4200	3.5—2.7	15.0
8400	2.7—1.9	11.0
13200	1.9—1.5	8.0
19200	1.5—1.2	6.0

REFERENCES:

- Taylor, Chaps. I and III.  
Getman and Daniels, Chaps. X and XIV.  
Millard, Chaps. II and XVI.  
Findlay, Chap. XXI.



## EXPERIMENT 42

### THE PREPARATION AND PROPERTIES OF COLLOIDAL SYSTEMS

The subject of colloid chemistry is concerned with the physical and chemical phenomena that arise from the dispersion of one kind of matter (termed the disperse phase) through another kind of matter (termed the dispersion medium) in such a way that the particles (solid, liquid or gas) constituting the dispersed phase have diameters that lie between the upper limit of molecular dimensions and the lower limit of microscopic visibility. These limits are approximately  $1\text{ m}\mu$  ( $= 10^{-7}\text{ cm.}$ ) to  $100\text{ m}\mu$ . Such a high degree of dispersion imparts to colloid systems a pronounced stability.

Various types of colloid systems are possible, depending upon the state of aggregation of the two phases. Thus, for example, a gas may be colloidally dispersed in a solid or a liquid medium; a liquid in a liquid, a solid or a gas; and a solid in a liquid, solid or a gas. Of the eight types of systems possible, the most familiar are the solid in liquid, the liquid in liquid, and the liquid in semi-solid. These are called respectively suspensoid sols, emulsoid sols and gels. The term sol is used to differentiate a liquid colloid system from a true solution, the essential difference being that in the former case we are dealing with single groups composed of many molecules, atoms or ions dispersed through a liquid medium, whereas in the latter case the molecules, atoms or ions are dispersed as individual units throughout some solvent. In consequence of the fineness of subdivision of the dispersed phase, sols in general appear to be homogeneous and in this respect at least superficially resemble true solutions. The lack of homogeneity, however, can be readily detected by means of the Tyndall effect of a beam of light, and frequently in the case of colored suspensoid sols by the difference in color when viewed in transmitted and reflected light, e.g., a red gold sol appears red in transmitted light and chocolate brown in reflected light.



Among the many interesting properties of sols may be mentioned the following: their slow diffusion velocities, low osmotic pressures, low electrical conductivities, remarkable structural colors, the fact that the dispersed phase is electrically charged with respect to the dispersion medium, the protective action of certain substances, and the effect of added electrolytes. These and other properties doubtless result from the fact that the principal energy form present in a sol is surface energy. That this must be of appreciable magnitude is evident from the following consideration. The energy factors of surface energy are interfacial tension (see Exp. 11, on surface tension) and interfacial area. The former is constant at constant temperature for a given system, but the latter increases enormously with increase in degree of dispersion. This is illustrated by the fact that a cube of any solid having an edge of 1 cm. has a total surface area of 6 cm.<sup>2</sup>, whereas the same mass and volume of material dispersed in smaller cubes having an edge of 1 m $\mu$  has a surface area of  $60 \times 10^6$  cm.<sup>2</sup>. This area multiplied by the interfacial tension yields a high value for the surface energy. In this connection it should be pointed out that the dispersion medium plays a very important part in determining the properties of the colloid system, as the surface tension is different for different liquids.

Since the colloidal state lies between that of fine suspensions and molecular dispersions, it should be possible to produce a colloidal system starting with either large aggregates of material or with true solutions. In the former case the degree of dispersion would be increased by breaking up the coarse material and in the latter it would be decreased by causing the ions or molecules to unite to form larger particles. Such methods are called respectively solution or dispersion, and crystallization or condensation methods. The condensation methods are much more numerous than are the dispersion.

The principal types of dispersion methods are (a) mechanical; (b) washing out; (c) electrical disintegration; and (d) peptization. The principal condensation methods are (a) reduction; (b) oxidation; (c) hydrolysis and (d) lowering of solubility.

In the preparation of a sol, electrolyte is generally either added directly or forms as the result of a chemical reaction. In any event it must be removed before the true characteristics of the



sol can be determined. This is best accomplished by dialyzing the sol. In the process of dialysis an arrangement is made whereby the sol to be purified is separated from a volume of pure water by a membrane permeable only to the water and the electrolyte ions and molecules. Under these conditions the direction of diffusion is such that the electrolyte molecules and ions leave the sol and enter the water. In dialyzing a sol it is well to change the water frequently in order to hasten the process.

Figure 69 shows the form of dialyzer used for rapid dialysis. A is a bell-jar having an opening at its top. A collodion membrane C is stretched across the bottom and is fastened by means of string wound around the flange of the jar. The cell thus formed is placed in a large crystallizing dish P containing water. The sol is carefully poured into the bell-jar which is then raised or lowered so that the stirrer S inserted through the top is about 1 cm. from the membrane. The motor M is started and the dialysis permitted to continue for about 24 hours with frequent changing of the water in the crystallizing dish. A small electric fan motor with a slide-wire rheostat in series makes an excellent stirring motor.

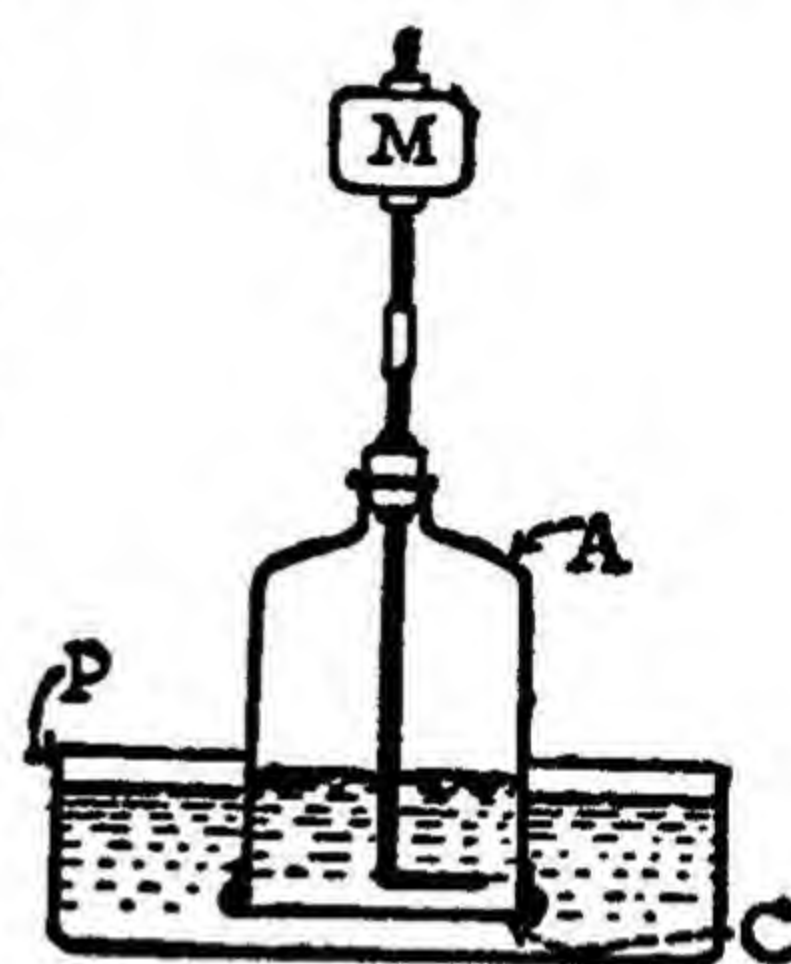


FIG. 69

The collodion membrane may be prepared as follows: Pour about 50 cc. of an ether-alcohol collodion solution over a surface of mercury contained in a crystallizing dish. In about 30 minutes the membrane should be dry enough to mount on the bell-jar. However, before attempting this, first carefully loosen a small section of the membrane at the edge of the dish and see if it can be lifted from the surface without tearing. When this can be done place the bell-jar on top of the collodion in the crystallizing dish and bend the loosened membrane up over the flange of the jar. Fasten the membrane to the jar by means of several turns of soft cotton string wound around that portion extending above the flange. The string must be wound carefully so as to avoid cutting the membrane. The bell-jar is then removed from the crystallizing dish and the membrane examined for holes. If free from holes the dialysis is carried out as described above. Care must be taken,



in testing the membrane for dryness, to prevent drops of mercury from getting on top of the collodion, since, when it is soft, these drops sink through and thus produce holes.

### (A) RED GOLD HYDROSOL

BY

ZSIGMONDY'S FORMALDEHYDE REDUCTION METHOD

(See W. W. Taylor, Chemistry of Colloids, 2nd Ed., p. 189)

First prepare the following solutions, using carefully distilled water and thoroughly cleaned pyrex glassware in each case. (a) 0.18 *N* potassium carbonate; (b) 0.3 cc. commercial formalin in 100 cc. water; (c) gold chloride solution prepared by dissolving 6 grams of crystallized chlorauric acid,  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , in one liter of water.

150 cc. of distilled water (good quality) is heated in a hard glass beaker and 2.5 cc. of the gold chloride and 3.5 cc. of the potassium carbonate solutions are added. When this solution begins to boil, heating is discontinued and 3–5 cc. of the formaldehyde solution is added at a rate of one drop every 20 seconds with thorough stirring after each addition. The reaction occurs rapidly after the addition of the first cubic centimeter of the reducing agent, changing the liquid from a light pink to a brilliant red.

Prepare about 450 cc. of this sol and dialyze for about 24 hours. According to Zsigmondy, this volume of sol is best prepared in three separate 150 cc. quantities rather than in a single operation. After dialysis preserve the sol, for later experiments, in thoroughly cleaned hard glass or fused quartz flasks.

### (B) HYDRATED FERRIC OXIDE SOL BY HYDROLYSIS

Heat about 300 cc. distilled water to boiling in a one liter hard glass beaker, and while the water is gently boiling slowly add with constant stirring 4–6 cc. of a 30–40 per cent  $\text{FeCl}_3$  solution. Remove from the heater and when cool dialyze for about 24 hours. The sol should be reddish-brown in color and perfectly stable. Preserve in a hard glass or fused quartz flask.



**(C) PREPARATION OF A GOLD AND A SILVER SOL**

BY

BREDIG'S ARC METHOD

(See W. W. Taylor, *Chemistry of Colloids*, 2nd Ed., p. 220)

Two gold and two silver electrodes are made by fastening 5 cm. lengths of gold and silver wire 1 mm. in diameter to copper leads. Each wire and its lead is pushed through a small glass tube about 6 cm. long, which serves as a handle and as an insulator.

Place a few cubic centimeters of distilled water in a small crystallizing dish and add a trace of a 0.5 *N* NaOH solution. Connect the leads of the two gold electrodes to a direct current line, protected with fuses (capable of carrying a current of 5–10 amperes at 30–110 volts). Form an intermittent arc under the water by momentarily bringing the wires together and then separating them slightly. When the water is appreciably colored, remove the electrodes and filter off any precipitate present. Compare this gold sol with that prepared in (A) above.

Repeat the above procedure, substituting the silver electrodes for the gold.

Note the electrode from which the metal is dispersed.

**(D) THE FLOCCULATION OF GOLD AND FERRIC OXIDE  
SOLS BY ELECTROLYTES AND BY EACH OTHER**

The stability of many colloidal systems, especially suspensoids, is considerably reduced by the addition of small quantities of electrolyte. When added in the correct proportion the electrolyte may completely precipitate the entire dispersed phase. It has been observed that in some cases certain electrolytes are more effective in bringing about such precipitations than others. This difference in action is related to the sign of the electrical charge of the dispersed phase, the nature of the added electrolyte, and the valency of the ion of opposite charge to that of the dispersed phase. This relation is expressed in the Hardy-Schulze valency rule and may be stated as follows: The precipitation of a sol is largely effected by the ion of opposite electrical charge and the effectiveness of this ion in bringing about the precipitation is a function of its valency. Thus one would expect a trivalent cation to be more effective in precipitating a negative sol than a uni-



valent cation. While this is true in many cases, there are enough exceptions to prevent the rule from being regarded as an exact law.

Test this rule by determining the precipitating power of sodium chloride, barium chloride, aluminum chloride, ammonium chloride, sodium sulfate and magnesium sulfate for the sols prepared in (A) and (B).

This can best be done as follows: Thoroughly clean and dry twelve 125 cc. hard glass Erlenmeyer flasks. In six of these place 25 cc. of the gold sol and in the remainder a similar volume of the ferric oxide sol. From burettes add 0.1 normal solutions of the electrolytes just mentioned, 3-5 drops at a time to each of the flasks, and determine the minimum concentration required in each case to produce precipitation. The sol should be thoroughly shaken after each addition of electrolyte and a time interval of 2 minutes should be allowed between successive additions.

Repeat the above experiment, substituting the ferric oxide sol for one of the electrolytes, and determine the quantity required for the precipitation of 25 cc. of the gold sol.

#### (E) DETERMINATION OF THE GOLD NUMBERS OF GELATIN AND TRAGACANTH

Substances such as gelatin, agar-agar, gum arabic and tragacanth, when added to a suspensoid sol decrease the effectiveness of electrolytes in precipitating the dispersed phase. This is called protective action and the substances producing it are known as protective agents. Their effectiveness is expressed in terms of their gold numbers. The gold number, according to Zsigmondy, is: the maximum number of milligrams of protective colloid that may be added to 10 cc. of a red gold sol without preventing a change from red to violet by 1 cc. of a 10 per cent sodium chloride solution.

The gold number may be determined as follows: Prepare a 0.1 per cent gelatin sol, and a 1 per cent tragacanth sol, by "dissolving" the required weight of these materials in the proper volume of water. Put 0.01, 0.1 and 1 cc. of one of these sols in three test tubes, and add to each 10 cc. of the red gold sol prepared in (A) above. After thoroughly mixing, add 1 cc. of a 10 per cent sodium chloride solution to each tube. If, for example, there is a color change in the 0.1 cc. and not in the 1.0 cc. sample, the gold number lies between these two. Now take 0.5



cc. of the protective sol, and determine whether the gold number lies between 0.5 cc. and 0.1 cc., or between 0.5 cc. and 1.0 cc. In this way, by systematically trying different volumes of the protective sol, locate the gold number to within 0.1 cc. or better. Knowing the concentration of the protective colloid, the number of milligrams present in this volume can be calculated.

Repeat this determination with the other protective agent.

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- Millard, Chap. XVI.
- Findlay, Chap. XXI.
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- Kruyt and van Klooster, *Colloids*.
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